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F & F, Research & Development Division

Experimental Station Laboratory

Progress Report

HIGH SOLIDS AIR-DRY FINISHES PRIMER FOR HAND-CLEANED RUSTED STEEL

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ABSTRACT

Technical requirements for the development of a premium performance primer for rusty steel have been considered. The performance of inorganic zinc on sand blast cleaned steel would be difficult to match with high solids primers on hand-cleaned rusty steel using the current primer technology. The best experimental system approaching the target performance is based on a proprietary aluminum flake filled primer, the use of which is restricted because of unknown toxicity of the key ingredients. Very high solids vehicles capable of curing by multiple mechanisms have been briefly scouted.

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INTRODUCTION

The basis of this report is the need for primers with improved corrosion resistance in finishes applications. In particular, one of the long standing need in the maintenance finishes has been a quick drying primer of premium performance for hand cleaned rusty steel. It is anticipated that an attempt to develop a premium performance primer for hand-cleaned rusty steel would form the basis of the metal-primer technology as it would encompass essentially all the critical factors that govern the performance of the primers.

OBJECTIVES

The overall objective of this program is to provide technological basis for the design and development of high solids, air-dry, low bake finishes for marginally clean surfaces. The immediate commercial target is the maintenance primer for hand-cleaned rusty steel with field performance level at least 80% that of Inorganic Zinc applied over sand blast cleaned steel at less than 75% of the cost of Inorganic Zinc.

SUMMARY AND CONCLUSIONS

- The performance of primer is a composite function of the vehicle properties and the pigmentation. Most of the recorded efforts at F&F were directed at optimizing the vehicles with the best known pigmentation (lead and chromates). Removal of these inhibitive pigments from primer suggests that a basic understanding of the mechanisms of corrosion and its control is essential before attempting to formulate a new primer.

- A fundametal review of the mechanisms of protection against corrosion by organic coatings indicated that a) organic vehicles alone provide only limited protection, b) excessive water is always present at the metal interface, c) the rate of oxygen permeation determines the corrosion rate and d) a good primer contains inhibitive pigments, corrosion inhibitors and/or sacrificial metal.

- Sacrificial corrosion protection afforded by "Inorganic Zinc" is difficult, at best, to match with other modes of corrosion control (barrier and inhibitor) commonly employed in primers based on organic vehicles. Among the epoxy primers studied, the best protection is obtained with zinc flake filled system. However, the presence of large amount of zinc results in poor intercoat adhesion under Imron® polyurethane enamel. A tie-coat of zinc-free epoxy vehicle (topcoat or primer) may enhance the utility of the system and needs to be evaluated.

- A new lead for the design of primer for hand-cleaned steel has been identified. It involves the use of Accelerator 808® dissolved in high boiling acrylic monomers as penetrant and aluminum flake filled Hypalon 30 as topcoat. Preliminary results confirm that the in-situ cure penetrant/primer based on an extension of "Quick-set" acrylic adhesive technology provided excellent protection approaching that of inorganic zinc. In order to exploit this lead commercially, it is essential to a) develop a non-toxic in situ cure penetrant and b) higher solids topcoat capable of initiating free radical polymerization of the penetrant. No attempt has yet been made to explore or confirm these hypotheses.

- A comparison of clear vehicles made from current alkyds, epoxies and moisture-cured aromatic isocyanate prepolymers suggests that a) epoxies and moisture cured aromatic isocyanate prepolymers are comparable in providing protection, epoxies having better blister resistance, b) alkyds soften excessively and disintegrate by film swelling. The use of aromatic isocyanate prepolymer is limited because of their toxicity and high water sensitivity during manufacture, storage and application.

- Low molecular weight epoxies cure with Ketimine, polyamide and phenolkamine resins at ambient temperature and provide high solids cure system (60% volume solids). None of the modifications to incorporate inert pigmentation (talc and micaceous iron oxide), inhibitive pigmentation (barium metaborate, and zinc molybdate), inhibitors (Sicorin AZ®) and clear penetrants improve the primer performance to that of inorganic zinc on sand-blast cleaned steel.

- Brief scouting effort for a novel ambient cure chemistry has resulted in a hybrid-cure high solids system (70% volume solids). It comprises of in situ cure of an air drying vehicle (preferably with some residual hydroxyl functional groups) in the presence of both reactive monomers (trimethylolpropanetrimethacrylate, 1,6-hexanedioldimethacrylate) and isocyanate prepolymers (Desmodur N-75 or E-21). Although prototype primer compositions tended to be too hard and brittle with very good corrosion resistance on rusty steel, the rate of cure and flexibility can be varied to suit maintenance application. Further effort is necessary to explore the system and establish regime of operation for the development of a functional product.

ACTION TAKEN OR PROPOSED

Three exposure series based on the systems studied in this work have been issued for field exposure at Beaumont, Texas. The results of these exposures would be summarized separately at the completion of the tests. Two prototype primers are recommended for further development and field exposure:

a) an alkyd-acrylic-urethane hybrid-cure primer (modify for improved flexibility).

b) zinc-flake filled epoxy primer with intermediate tie-coat of zinc-free vehicle (eliminate intercoat adhesion with zinc-flake containing primer).

PATENT SITUATION

FF-3273 - Request for Filing a Patent on a proprietary primer composition based on "Quick-Set" in-situ cure penetrant has been made. Further action is deferred because of insufficient interest in the product at the present time.

Request to file for a patent on alkyd-acrylic-urethane high solids ambient-cure composition is deferred pending full assessment of its potential to meet F & F needs.

PUBLICATION STATUS

There are no plans to publish any of the results from this project.

TOXICITY, HANDLING AND SAFETY CONSIDERATIONS

Given all favorable conditions, if a successful high solids product (= 80-90% performance of inorganic zinc) is developed, it is highly probable that it would involve a) low molecular weight, reactive, multi-functional monomers, additives or diluents and b) some toxicological limitation on their use as spray applied primer. Primary ingredients of potential handling and toxicity hazards in the present study have been

a) Epoxy curing agent Ketimine H-3 which produces diethylene-triamine (DETA) on exposure to moisture. Ethyleneamines such as DETA are known to be skin-irritant and sensitizers and should be handled in a manner similar to that of Imron® line of finishes.

b) Molybdate containing pigments. There is some concern about the toxicological safety in the use of molybdates and require protective equipment to eliminate particulate hazard.

c) Corrosion inhibitors are of a variety of forms and some of their unique structures could also pose toxicological questions such as in the use of lithium benzoate, zinc dibenzylthiocarbamate and amines.

d) Isocyanate prepolymers, such as Desmodur N-75 and Desmodur E-21, are moisture reactive resulting in a variety of products with questionable toxicity. Desmodur E-21 in particular requires attention in that its reaction byproduct and intermediates can be highly undesirable aromatic amines. One must be alerted to metabolic influences when moisture-cured isocyanates are considered.

e) The use of polyfunctional methacrylate monomers requires full assessment of the level of their use in the finished formulation and its influence in skin-sensitization under conditions of use.

It is recommended that any high solids formulation for the rusty steel be tested thoroughly for toxicological data so that appropriate protective equipment could be specified for field application conditions.

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DISCUSSION

I. BACKGROUND

High performance primers are identified by the presence of red lead, chromates or zinc dust in most instances. Yet there is no completely satisfactory product based on these pigments and known vehicle systems that provides long term protection on hand-cleaned rusty steel. The history of research efforts on "new" primer for this end use in F & F is long (Appendix I) and yet the need for a quick-drying, premium performance primer on hand cleaned rusty steel remains. Red lead pigment in linseed oil alone, or in combination with alkyd resins has been the standard maintenance primer for use on hand cleaned steel. The system is slow to dry and it requires a quality topcoat for good protection. Further, the application of high quality, premium performing topcoats (such as Corlar® and Imron®) requires extended recoat interval over such primers and this delay in field use conditions is economically undesirable.

The primary effort in the development of new primer was in most cases concentrated on the vehicle development. Major raw material suppliers and new vehicle manufacturers also concentrate on promoting new resins for improved performance of primers. Such vehicle modifications are the easiest to incorporate and provide "proprietary" primers when formulated with corrosion inhibitive pigmentations. However, the design of new vehicles was, on the large part, aimed at improving adhesion, drying and weathering characteristics with incidental improvement in corrosion performance.

On the other hand, considerable strides have been made in the science of corrosion and extensive literature exists (1-3) An analysis of the corrosion phenomena suggests that the protection can be designed by either one or the combination of the following:

i) Physical Barrier (high film build)

ii) Electrochemical Barrier (sacrificial anode)

iii) Chemical Barrier (inhibitors)

A brief discussion of each of the controlling phenomena would follow to bring the problem of priming rusty steel surface in perspective.

Physical Barrier: One of the main modes of protection of steel from aggressive environments by polymeric coatings is of isolating the two by means of a physical barrier. In systems protected purely by this mechanism, the rate of attack on the metal is then governed by the fundamental laws of diffusion and transport

of oxygen, water and corroding ions through the coating to the metal interface. An examination of the permeability of organic systems (Appendix II) indicates that most of the polymers are too permeable to water and oxygen. Various investigators have examined this problem in detail and concluded that

a) organic vehicles alone provide limited protection, limited by high permeation of oxygen, water and ions because of molecular interactions, solubility and voids.

b) excessive water is always present at the interface and it causes adhesion loss as a prerequisite for the start of the corrosion process.

c) oxygen permeation is the slowest process. It controls the rate of corrosion and determines the acceptable life of the coating.

d) inorganic coatings such as those formed in metal treatment processes have much reduced permeability but their utility is limited to thin film applications because of excessive brittleness in heavier builds.

Advantage is taken in maintenance finishing of this mode of control by providing as high a total film build as economically possible, often between 5-10 mil dft. Most inert polymeric vehicles do not provide adequate physical barrier at this level of film build and require added protection by other modes of protection.

Electrochemical Barrier: It is well established that corrosion in aqueous electrolytes is an electro-chemical process. The corroding metal leaves the metallic state at anodic areas and consumes some constituent of the electrolyte at the cathodic areas. The rate of corrosion corresponds faradically to the current passing between the anodes and cathodes:

At The Anode:

$$M \text{ (metal)} \longrightarrow M^{++} + 2e$$

At the Cathode

(in acidic media) $O_2 + 4H^+ + 4e \longrightarrow 2H_2O$

$2H^+ + 2e \longrightarrow H_2$ (g)

(in neutral or alkaline media) $1/2\ O_2 + H_2O + 2e \longrightarrow 2(OH)^-$

These simple reactions are the basis of control by electrochemical and inhibitor means. In a cathodic control, the rate of corrosion is controlled by the rate at which the cathodic reaction could take place. In most cases of cathodic control, oxygen diffusion controls

the corrosion rate. The rate limiting step in an anodic control system is the dissolution of the metal which could be influenced by partially obstructive films on the metal.

Corrosion, being an electrochemical phenomenon, is accompanied and accelerated by the passage of very small electric currents between the corroding metal and any other metal with which it is in electrical contact or between different areas on the surface of the corroding metal. Two requisites for these currents to flow are:

a) A potential difference either between the two pieces of metal or between the different parts of the same piece. Potential differences sufficient to cause current flow arise from very small local inhomogeneities in the chemical constitution of the surface such as phase differences across a grain boundary, inclusion of sulfur, phosphorous and chlorides.

b) Presence of moisture or other electrolyte on the surface to act as a conductor for the current.

The direction of the current which flows when two metals are brought into contact in the presence of an electrolyte depends on the relative positions of the metals in the galvanic series. Anyone of these metals/alloys will theoretically corrode while offering protection to any other which is lower in the series, so long as an electrical continuity is maintained. Thus in the case of zinc and steel, a corrosion current will flow from steel to the zinc so that zinc becomes an anodic electron producing area while the steel is cathodic electron consuming. The zinc, therefore corrodes in performance to the steel and in so doing protects the steel surface. This type of "sacrifical or cathodic protection" occurs when zinc coatings on steel surfaces are subjected to mechanical damage, such as scribed mark with metal cutting tool, whereby the continuity of the zinc coating is broken and the steel surface is exposed.

This important property of zinc as a coating material (or a major coating ingredient), is also possessed, although to a lesser extent by aluminum. Direct application of zinc in processes such as hot dip galvanizing, zinc plating, spray metallizing are widely practiced for the protection of steel. However, zinc-rich coatings are used in the maintenance finishes where such processes can not insure full protection over the entire life span of the structure. Zinc rich coatings are often highly filled with zinc dust (80-95% by weight) and can be defined by their electrical conductivity. The interesting fact to note is that zinc rich primers perform universally much better than the best non-zinc primer in most

environments with the exception of highly acidic or alkaline environments. The sacrificial protection afforded by zinc is so overpowering that any system designed to replace zinc must provide essentially complete protection. It is, thus, important to stress that any attempt to make a primer for rusty steel must not exclude the use of zinc from consideration.

Chemical Barrier: Protection against corrosion requires that the continuity of the electrochemical cell be disrupted. In order to inhibit corrosion, it is necessary to stop the flow of current, either by suppressing the cathodic or the anodic reaction or by inserting a high resistance in the electrolytic path of the corrosion current. These three modes of control by suitable chemicals form the basis of inhibitor technology. Extensive literature is available that focuses attention to this mode of corrosion control in various industries; such as boiler-feed water, cooling water, oil drilling fluids, engine lubricants, metal cleaning and metal treatments. However, the use of inhibitors as a part of the coating is only recently recognized. The toxicity concern about the most widely used chromates for corrosion control has focused attention of various investigators to search for non-toxic replacements. It is anticipated that these efforts would identify specific inhibitors for the desired applications and most likely cannot offer essentially universal protection afforded by chromates. The science and technology of corrosion inhibitors has been summarized in the Appendix IV and discusses fundamental considerations for exploiting this technology. The successful development of non-zinc (or aluminum) primers with predictable performance requires understanding the role of inhibitors in the coating. Needless to stress that this is the least understood phenomena in the coating industry.

II. SPECIFIC CONSIDERATIONS FOR PRIMER FOR HAND-CLEANED STEEL

The problem of preventing corrosion in steel is still present in the case of hand cleaned rusty steel. The marginal cleaning of the surface creates additional difficulties:

a. The surface profile of hand cleaned surface depends on the extent of cleaning and could average between 4-6 mils. A very fluid gap-filling primer would fill in the valleys and provide only marginal coverage of the peak areas. A thixotropic composition provides somewhat better control of dry film thickness at the expense of reduced penetration and gap filling efficiency.

b. The rust and mill scale can provide good protection when impregnated with good wetting primer vehicle. Essentially, complete arrest of the corrosion process by the primer is essential and the primers are noted to fail precipitateously (peel-off) once the under film corrosion starts. This reasserts the importance of using zinc-rich or primer with good rust inhibitors. This is contrasted with primers on clean sand blasted surfaces where corrosion

can be tolerated to a higher extent before complete failures occur. Most coating systems, except for zinc-rich primers, do not offer such protection and are limited by the state of the coating technology.

c. Rusting in a chemical environment leaves contaminations that may accelerate corrosion. The level of contamination is determined by the amount of rust and mill scale left after hand cleaning. The type of contamination is influenced by the environment in which rusting occurs. An inhibitor capable of making such contaminants harmless would add to the service life of the primer.

d. The porosity of the rusty surface tends to extract the vehicle out of the primer resulting in an uneven distribution of the pigment in the primer. The highly filled primers (close to CPVC) could result in too porous primer (dry look) and fail because of large voids through which water, oxygen and corroding ions may migrate readily. It is therefore desirable to pigment the primer at 30% or lower PVC.

e. In field applications, the primer for rusty steel requires it to be applied not only to all rusty surface but also to partly rusted and partly residual paint bearing surfaces. This type of field substrate conditions are variable and difficult to reproduce. The success in the commercial use depends on the versatility of the primer application to a variety of surface conditions.

III. STANDARD OF PRIMER PERFORMANCE

The current standard of primer performance in maintenance painting is Inorganic Zinc (IOZ) applied over "white" metal (sand blast specifications SSPC-10). Following characteristics are considered necessary for a suitable primer for hand cleaned steel:

- Performance level 80-90% that of IOZ (applied on "white" metal)
- Rapid dry and cure for recoat in less than 4 hours with topcoats containing active solvents
- Non-chromate and lead free pigmentation
- High solids (preferably as high as 70-80% volume solids) with air pollution conformance regulatory classification being such that it may be used anywhere in the U.S.
- Applied cost at not more than 75% than that of IOZ.
- A unique proprietary product would command both a premium price and a large market share

IV. DEVELOPMENT STRATEGY

Above discussion of the corrosion controlling mechanisms, the special problems of painting rusty steel and the failure of numerous attempts to make a commercially successful primer indicates that the target performance of 80-90% that of Ganicin® 347-931 (IOZ) on sand blasted steel would be difficult to achieve. It was therefore necessary to consider a developmental strategy so that incremental improvement in the performance can be identified. Following is such a scheme for primer for hand cleaned steel.

a. Develop chromate-free primer equivalent to the performance of Corlar® 825-8031 on blast cleaned steel.

b. Assess feasibility and develop high solids analog of (a).

c. Develop chromate-free, zinc-containing primer equivalent to the 80-90% performance of Ganicin® 347-931 on blast cleaned steel (target performance).

d. Assess feasibility and develop high solids analog of (c).

e. Develop proprietary zinc and chromate free primer for target performance.

f. Assess feasibility and identify high solids analog of (e).

This sequential execution of the program is logical, more realistic, likely to provide a technical basis for widely applicable primer technology and may offer primer candidates capable of direct substitution in place of current commercial analogs for use over rusty steel. These intermediate levels of performance were not judged to be good enough for introducing new primer for rusty steel. Also, time and resource constraints could not justify completion of each of the intermediate steps. The objective of the program was, therefore, to attain (f) without necessarily developing intermediate candidates.

The development of primers for maintenance finishes has been more an art than a science and there is not defined procedures for identifying a primer system. Following developmental strategy was adopted to ensure a balance between longer term D.I.E.B. effort of providing a technological basis and short term I.E.B. effort to develop a functional primer for rusty steel.

a. Assess the role of common vehicles such as alkyds, epoxies and urethanes in primers.

b. Establish the role of inert pigments in the selected vehicles.

c. Evaluate inhibitive pigments in combination with inert pigments in the preferred vehicles.

d. Formulate prototype primers and compare their performance characteristics with current commercial primers, including Ganicin® 347-931 (IOZ).

e. Evaluate inhibitors (non-pigment additives) and compare their effectiveness versus non-toxic inhibitive pigments.

f. Evaluate the role of reactive and nonreactive penetrants in prototype primer vehicles.

g. Select a preferred candidate and assess marketability of the product based on its performance, application characteristics, cost and profitability.

A. Role of Vehicles

An exposure series (Appendix IIIA) was prepared from a number of commercial primers (as controls) and their clear vehicles, experimental epoxies cured with a variety of curing agents and aromatic isocyanate prepolymer (Desmodur E-21). Three substrates used were (a) polished clean cold rolled steel; (b) hand cleaned rusty cold rolled steel and (c) hand cleaned rusty hot rolled steel. The primers were applied at 2-mil dft with 2-mil dft topcoat of 369Y-67641 and exposed for 500 hours salt spray. Low film thickness and shorter exposure time was considered to be desirable to differentiate between various systems. Following observations were made:

- Corlar® (825-line) and Dulux® 67-746 are good primers for clean steel showing very little creepage from the scribed line but poor on rusted steel.

- Corlar® clear vehicle shows severe undercutting at the scribe on clean-cold rolled steel (C-CRS) but reduced visible undercutting on rusted panels, indicating that a combination of lower viscosity vehicle and the presence of rusty layer protects better than the commercial pigmented analogs. While the differences were small, it was noticeably obvious that the clear vehicle had improved penetration and wetting of the rusty layer compared to the pigmented analog.

- Clean polished steel surface is more active and tends to corrode faster than rusty steel. This trend was seen in major part of the series.

- Dulux® clear vehicle shows complete failure, essentially disintegrating badly over the three substrates. The presence of chromate pigmentation in both the Dulux® primer 67-746 and Corlar® 825-8031 clearly offers marked corrosion protection and film reinforcement. The alkyd films are still very weak and saturated with water as compared to Corlar® epoxy-polyamide vehicle.

- Inorganic zinc (Ganicin®) 374-931 control on C-CRS was perfect with no failures at all. The clear vehicle does not form film on steel. Distinction must, therefore, be made between organic primers filled with pigments and inorganic primer where zinc is the reinforcing part of the matrix.

- Experimental epoxies were all comparable in performance on all the substrates. Ketimine (H-3), aromatic amine adducts (Araldite 830 and Araldite 850) and polyamide (Versamid 280B75) were selected for further testing of pigmented compositions.

- Aromatic isocyanate prepolymer (Desmodur E-21) also performed equivalent to the epoxies but exhibiting slightly greater tendency to blister.

The role of vehicle is thus to provide primarily the application latitude, cure, dry time, good adhesion etc. and only incidental improvement in corrosion protection. It was expected that suitable pigmentation can upgrade the performance of high solids experimental systems.

B. Role of Inert Pigmentation

Low molecular weight epoxies cured with ketimine, polyamide and polyamine (Appendix IIIB) were pigmented with talc and micaceous iron oxide. An exposure series No. 24216 with commercial control was prepared. The results of salt spray cabinet testing after exposure for 1500 hours showed the following trends:

- Dulux® 67-746 on C-CRS (control, #6-1) and R-CRS and R-HRS (#6-11) shows dense blistering both in primer and topcoated section. The primer film is very weak and soft because of excessive water retention.

- Corlar® 825-8031/VG-88339 on C-CRS (control #6-2) performs excellent but fails on rusted panels (#6-12) by dense blistering and overall rusting.

- Low molecular weight polyamide Emerez 1514 cured epoxy primer (848-E-139, panel #6-9) failed by dense blistering, probably because of inadequate cure or application.

- All other experimental candidates on rusted panels exhibited comparable performance to that of Corlar® 825-8031/VG-88339 on C-CRS.

- Following candidates with talc and micaceous iron oxide pigmentation were judged to be slightly superior to other experimental candidates:

  848-E-135-3C Epoxy/Ketimine Adduct (#6-6)

  848-E-141 Epoxy/Polyamide Adduct (#6-10)

  848-E-137 Epoxy/Polyamide Adduct (#6-7)

These would be studied further.

- Ganicin® 347-Y-931 continued to show excellent performance on both SB-HRS and R-HRS.

- Aluminum flake filled epoxy/ketimine adduct primer shows excellent performance.

- 20% PVC appears to be adequate for primers over rusty steel. A candidate (848-E-144, panel #6-14) pigmented at 30% PVC showed adhesion loss between primer and Imron® topcoat when exposed to salt spray.

- Re-examination of the experimental test panels after 3 months of storage showed extensive under film rusting. Epoxy/phenalkamine (848E-138) cured system did not show this failure and was included for further studies with inhibitive pigments.

It can be summarized that a purely physical barrier of cured epoxies filled with talc and micaceous iron oxide pigment at nominal primer thickness of 4 mil does not afford the needed protection. It is due to the absence of both chemical or electrochemical corrosion controlling mechanisms. It is interesting to observe that IOZ (Ganicin® 347-931) performs excellent on SB-HRS and relatively good on R-HRS, again confirming the dominant role of zinc in controlling corrosion even though it is not in direct physical contact with the steel but electrochemically connected by the conductive electrolyte in the porous rust. It must be recognized that zinc retains its effectiveness both in small concentrations and when isolated from steel by short distances. However, direct electrical contact of zinc with metal will decidedly improve corrosion performance.

A separate study (Exposure Series #24217) was conducted to examine the influence flake pigementation. The flake pigments included are shown in Appendix IIIC. Ganicin® 347-Y-931 was used as control. The results of 1500 hours salt spray indicate that a) inert flakes such as glass, mica and talc are not suitable as the pigments for primers for hand cleaned rusty steel in the vehicle examined, b) the system with zinc-flake shows good performance on C-CRS with spot failures on R-HRS suggesting that the zinc flake can potentially be used in organic vehicles to provide both barrier and electrochemical protective control, c) aluminum flake containing epoxy/ketimine primer fails by blistering at the scribe and edge rusting.

It thus becomes apparent that although epoxies are commonly used primer vehicles for clean substrates, they are poor performers over rusty steel with inert or flake pigmentation, the substrate being continuously variable shows variable performance.

C. Role of Inhibitors and Inhibitive Pigments in Primers

Inhibitors offer chemical means to intercept corrosion reaction and impart a rate limiting step, thereby controlling the useful life of the coating. Numerous literature references (Appendix IV) suggest a variety of inhibitors but their utility in paints has not been established. Inhibitor technology, as applied to primers is in its infancy, primarily because of dominating impact of chromates as to their availability, effectiveness and price. There is sudden realization throughout the industry of the need to understand and exploit the inhibitor technology when the use of chromates is severely curtailed by law. The technology of inhibitors appears critical in the development of new high performance metal protective systems, especially where low cost alternatives to the use of zinc metal is considered. However, a meaningful understanding of this technology would require concerted effort on an on-going basis and was beyond the scope of current effort. Some of the recommendations are outlined in Appendix IV.

Of the large list of potential inhibitors only two were examined in the epoxy/ketimine primer at 20% PVC (talc and micaceous iron oxide) with 10 phr of the inhibitors:

Zinc bibenzyldithiocarbamate (Arazate) and Lithium Benzoate

The results of salt spray testing (1600 hours) confirm that both the inhibitors considerably retard the underfilm corrosion to a point where the performance of epoxy primers on hand cleaned rusty steel can be compared to that of Corlar® 825-8031 on sand blasted steel. Since these two chemicals were not designed for use in this manner, there is reason to suspect that both contain water soluble salts which introduce water sensitivity in the coating as evidenced by very fine blisters. Both these chemicals appear as effective inhibitors in the primers examined, though not entirely satisfactory for use in any commercial system.

Initial success with the two selected inhibitors suggests that a wide variety of chemicals can behave as inhibitors. It is recommended that a separate study of inhibitors for use in alkyds, epoxies and urethanes be conducted. Identification of electrochemically effective inhibitors can provide proprietary position as well as offer system at the lowest cost.

The primary emphasis by pigment suppliers has been the introduction of non-chromate corrosion inhibitive pigments. A list of such pigments is included in Appendix III. Most of these are not as univerally applicable as chromates and show varying degree of effectiveness in common primer vehicles. A number of F & F programs have examined these new pigments. Jim Courtright(4) in his effort to develop chromate-free analogs of Dulux® and Corlar® primers found barium meta-borate (W-178, Busan M11) and zinc molybdate as the preferable pigments in the epoxy primers. These two pigments and two prototype inhibitors were therefore included in a composite one shot effort of examining the performance of the epoxy primers with the best known pigmentation and all other approaches to primers for hand-cleaned steel. The results of this exposure series are summarized in the following sections.

D. Other Approaches to Primers for Hand-Cleaned Steel

- Penetrant-Primer Systems: Linseed oil penetrant under an alkyd (Dulux®) or epoxy-polyamide (Corlar®) primers for application on hand-cleaned rusty steel is frequently used. It is not clear whether this really upgrades the system performance. This mode of primer application i.e. mist coat of penetrant followed by primer topcoat was used to an advantage in a modification of "Quick-set adhesive system" (7). The primer system is based on Accelerator 808®/acrylic monomer blend, used as penetrant, which on contact with aluminum flake filled Hypalon® rubber initiates in-situ free radical polymerization of the acrylic monomers. An exposure series was prepared based on few modifications. Following conclusions were drawn based on 2000 hours salt spray exposure.

- Penetrants based on 10% Accelerator 808® and 90% acrylic monomers or epoxy diacrylate (XD-9002) show excellent performance. The blend should be homogeneous for optimum effectiveness. For spray application the solids level of penetrant can be varied between 20-60% (by wt.). Two penetrants were noticeably superior:

Reference: 878E-39-3: Acc-808®/BMA/XD-9002//10/60/30 @ 60% S
878E-39-5: Acc 808®/XD-9002//10/90 at 43% S

- Aluminum flake filled in-situ cure Hypalon® primer has shown outstanding corrosion resistance meeting the performance objectives of the program (80% that of Ganicin® on sand blast cleaned steel).

● The system is essentially of low solids (30% weight solids) and could pose toxicity hazard of spray applying Accelerator 808®/monomer blend. The use of aluminum flake in chloro-sulfonated polymer has also been questioned as to its potential of spontaneous exothermic reaction. This system is, therefore, no longer under consideration. However, it is likely that non-toxic system based on this approach can be identified and provide a proprietary patent position (Appendix V).

b. Modification of Existing Products: The present primer for hand cleaned steel is Dulux® 67-746 (chromate-containing linseed oil modified alkyd). The main weakness of this primer in affording extended protection lies in its vehicle being too easily saponified and poor integrity. A lead, based on the work of Heiberger[5] and Leavell[6], of modifying air-drying alkyds with acrylic monomers (e.g. Trimethylolpropane trimethacrylate) was studied briefly to upgrade the performance of this primer. 50% dilution of Dulux® 67-746 with TMPTMA gave a 77% volume solid primer exhibiting very good performance on rusty steel after 1500 hours salt spray. The two limitations were recognized.

a. Continuation of the use of chromate pigmentation, and

b. Slow dry (16-24 hours)

A variety of other modifications have since been made (Appendix VI) with varying degrees of pot life and dry times in systems free of chromate pigmentation. It was observed that considerable formulating latitude in controlling the cure, dry time and pot life of their acrylic modified oxidativity air-drying vehicles exists. Scouting effort (Table III) has shown that the anti-skinning agents (MEK-oximes) and polyisocyanate prepolymers in the presence of driers provide a multitude of cure mechanisms to control the pot life and dry time of the primer. These high solids vehicle modifications are of little utility unless inhibitive pigments and inhibitors can be incorporated to give a formulated primer. Prototype primers with the best known pigmentation were therefore prepared (Exposure series #24323) to compare their performance on hand cleaned steel relative to Ganicin® 347-931 on sand blast cleaned steel (Appendix IIID).

V. CONCLUSIONS AND RECOMMENDATIONS

● The performance of a primer is a composite function of the vehicle properties and the pigmentation. Most organic vehicles alone can not provide adequate corrosion protection because of excessive water and oxygen diffusion and lack of corrosion inhibitive properties.

- Inorganic Zinc (Ganicin® 347-931) on sand blasted steel is the premium performance primer and can not be compared with most primers considered in this report with the following exceptions:

(a) Zinc flake 21HF filled epoxy (75% weight solids, 63% wt. zinc flake at 30% PVC) at 80% the cost of inorganic zinc.

(b) In-situ cure Accelerator 808® (pentrant) activated aluminum flake filled Hypalon 30 primer (27% weight solids) at 80% the cost of inorganic zinc.

- Inhibitors can upgrade the performance of primers by retarding the corrosion kinetics. Prototype inhibitors were functional in epoxy primers at 10 phr. High potency inhibitors may be identified but it remains doubtful if the performance level of IOZ can be achieved entirely by their use.

- Epoxy primers without chromate pigmentation are limited to a maximum of 60% volume solids for spray applications. The vehicle cannot penetrate and wet the rusty pores adequately to arrest under-film corrosion starting at the scribe. Highly effective chromate free inhibitors or the presence of sacrificial zinc in the coating is essential to approach the target objective of 80% performance of Ganicin® 347-931.

- A high solids in-situ cure primer with built-in penetrant is derived from Dulux® 67-746 modified with TMPTMA (50% by weight) to yield a high solids (77% vol. solids) primer with performance level better than the unmodified alkyd primer. Further modification with other acrylic monomers and isocyanate prepolymers have been discussed as a means of controlling dry time, pot life and cure of the primer. There is definite need to refine the prototype formulations for optimum cure and compatibility before any commercial analogs could be developed.

- Epoxy/phenalkamine system provides a more complete cure (vs Epoxy/ketimine) as judged from the increased blister resistance of the primers with the same inert pigmentation. This, of course, yields primer of less than 60% vol. solids.

- There is no basic understanding of whether a particular inhibitive pigment would perform satisfactorily. In addition, most of the available information refers to the case of priming sand blast cleaned steel and of limited value to the present study. A primer for hand cleaned steel requires absolutely perfect corrosion control system, such as inorganic zinc on sand blasted steel, to be effective. The technology of developing such a product requires a systems approach to incorporate all the corrosion controlling phenomenon. Such an effort could not be made for the lack of understanding of both corrosion control and new air-dry high solids curing systems.

- The technology of inhibitors is in infancy and holds promise. There is no active program in F & F and chances of success are limited. It would be worthwhile to monitor field developments closely, particularly the reports from Inhibitor Technology Subcommittee of National Association of Corrosion Engineers.

- Most of the developmental work in the past and in the current program was limited to common primer vehicle chemistries. An added awareness of the importance of the corrosion inhibition process suggests that once the technology of chemical control of corrosion is established, it would be logical to design primer vehicles with built-in inhibitor functionalities. The success with the use of Accelerator 808® confirms to its multiple role as a penetrant, free radical initiator, wetting agent, adhesion promoter and corrosion inhibitor. Although the toxicity of spray applied Accelerator 808® is not established, it would be desirable to consider potentially less toxic analogs such as that made from dodecylamine and butyrldehyde.

This study has barely touched the main issues important in the development of the primers. It has not evolved the solutions but only identified the areas of expertise needed to develop a strong product and proprietary advantages.

RTK:lms

REFERENCES

1. Shreir, L. L., Corrosion, Volumes 1 & 2.

2. Uhlig, H. H., Corrosion & Corrosion Control

3. Collected lectures on Corrosion & Protection of Metals, Published by American Elsevier.

4. J. R. Courtright, Report No. TF-76-9.

5. P. H. Heiberger, Report No. TF-78-1.

6. K. H. Leavell, Report No. EX-78-1.

7. J. M. Craven, Report No. EX-75-21C.

TABLE I

PENETRANTS FOR IN-SITU CURE ALUMINUM FLAKE FILLED HYPALON® 30

Reference: 878E-39-	2	3	4	5
Accelerator 808®	10	10	10	10
Butyl methacrylate	90	60		
Lauryl methacrylate			60	
Epoxy diacrylate, XD-9002		30	30	90
MEK	20	6	6	18
Cellosolve Acetate	30	30	30	30
Xylene	100	30	30	90
Total	250	166	166	238
% Solids (wt.)	40	60	60	42
Appearance	Clear	Clear	Cloudy	Clear

QUICK-SET CURE

"Reactive, In-Situ Vinyl Cure"

Lead: Quick-Set Adhesives

Characteristics: Apply Activator to one surface (even oily)
Apply Adhesive to the other surface (Hypalon® 20/30 in MMA/MAA)
Join, Exclude air
Set time 5 minutes
Cure up to 25 mils+
Bad Odor
Toxicity (MAA)

Coating Application:

Penetrants:

Accelerator 808®
Epoxy Diacrylate XD-9002
Reactive diluent (non-volatile, low volatility solvent, non-toxic)
Apply wet coat

Primer:

Hypalon® 30
Aluminum Flake, W-128
Hydrocarbon Solution
P/B 67/100
Apply Over Wet Penetrant

TABLE II

HIGH SOLIDS AIR DRY ACRYLIC MODIFIED ALKYD PRIMERS WITH ISOCYANATE PREPOLYMERS

Reference 878E-	-68-1	-141-II	-69-1	-148-I	-148-II	-146-1	-146-2
Air dry oligomer 786E-30						20	20
Dulux® 67-746	164.0		7.54				
Dulux® 67-H-43034				164.0	164.0		
Primer Mill Base 878E-148				90.82	90.82		
TMPTMA	53.0	1	2.44	33	32.1		
XD-9002		1					
1,6 HDDM							
Epoxy-ester 786E-68		5	5.0				
BGDMA				40		20	20
H-44		4					
H-172		0.5	0.02			0.1	0.1
H-49			5.0				
VG-Y-518				30		20	
Des E-21					20		20
H-79						15	15
% Solids (wt)	87.53	54.5	64	85.3	85.5	73.3	80.0
(vol)	77			70+	70+		
PVC	23.5	Clear	14.3			Clear	Clear
Mix Ratio	2:1						
Dry Time, Hrs.	24	7	4	6	1	3*-12	0.5*-1.5
Gel Time, Hrs.	>24	>24	>24	>4	1		

*with additional drier

cc: S. G. Smith - F&F - Marshall Laboratory

APPENDIX I

CENTRAL REPORT INDEX
3211 CENTRE ROAD BUILDING
WILMINGTON, DELAWARE 19898
Information Systems Department

November 12, 1975
CRI Ref. No. W-75-5342
Request Rec'd. November 6, 1975

TO: R. T. Khanna
Fabrics & Finishes
E 293/202

FROM: P. J. Sazegar, Supervisor
3219 Centre Road Building
Ext. 4113

P. J. Sazegar

MAINTENANCE PRIMERS: FABRICS AND FINISHES
DEPARTMENT REPORTS ONLY

Eighteen summary and conclusions are enclosed on the title subject.

Departmental Rept. No.	Departmental Rept. No.
R-56-45	R-62-16
R-62-26	R-62-32
R-62-33	R-62-34
R-62-43	R-62-78
R-63-6	R-64-31
R-66-58	R-68-29
R-68-89	R-69-38
RM-62-5	RM-62-11
RM-63-2	SM-64-7

S. G. Smith sent you thirteen references which I'm listing below just for completeness of the search answer. No summary and conclustions are sent for these reports. Many references in this group are basic information studies on corrosion. I found no additional information in this area which I thought would be of interest.

ESR-58-18	R-61-32
ESR-59-4	R-62-12
R-55-1413	R-62-42
R-56-46	R-62-93
R-57-38	R-64-14
R-58-26	RM-57-5
R-61-28	

R.T. Khanna
CRI W-75-5342

November 12, 1975

I found reference to five additional reports, but, unfortunately, we do not have microfiche copies of these reports. Possibly you may wish to check with S.G. Smith on this matter.

1339	R-56-26
1399	R-57-58
1413	

Please feel free to call on me if you have questions or require additional help.

Enclosures
PJS/reb

APPENDIX II

O_2 AND H_2O PERMEABILITY OF POLYMERS AT 25°C

POLYMER	O_2 AT 0% R.H. P x 10" cc-cm/cm^2 sec cm Hg	WATER P x 10" g cm/cm^2 sec cm Hg
p-VA	∿0.0001	∿5000
pVDC	0.012	∿0.052
NYLON 6	0.062	19.5
p-CHLOROTRIFLUOROETHYLENE	0.18	0.19
PET	0.42	3.2
PVC	0.48	2.5
pMMA	1.0	13.7
pVAc	3.3	107
p-ETHYLENE (LINEAR)	5.4	0.21
CELLULOSE TRIACETATE	7.2	291
POLYPROPYLENE	10.8	0.42
POLYCARBONATE	13.5	20.8
p-STYRENE	24.9	14.5
p-ETHYLENE (BRANCHED)	30.0	0.83
CAB	55.8	360
p-ISOBUTYLENE	90.0	9.2
p-BD	228.0	11.4
p-4-METHYL PENTENE-1	240.0	7.7
p-DIMETHYLSILOXANE	∿3000	80.5
MOISTURE-CURE TAR/NCO		0.53
EPOXIDIZED TAR/AMINE		0.85
URETHANE (PIGMENTED)		1.1

RTK:ayk
2/3/76

O_2 PERMEABILITY THROUGH COMMON PAINT FILMS

10^{-3} mg/cm^2/day

VEHICLE TEMPERATURE °C	10	20	30	40	50
CELLULOSE NITRATE	69.3	105.8	149.8	237.0	3.8
ALKYD - MF	4.2	10.3	19.2	30.3	50.6
EPOXY	4.7	7.3	8.6	17.8	33.7
VINYL AIR DRY	3.9	7.5	10.5	29.9	37.5
BAKED AT 60°C	4.1	4.9	6.4	10.7	19.0
CHLORINATED RUBBER	1.1	2.2	3.4	4.3 (45°C)	15.9 (60°C)

APPENDIX IIIA

PRIMER DEVELOPMENT FOR MAINTENANCE FINISHES

2 mil DFT Primer + 2 mil DFT Topcoat 369-Y-67641

System Description		Salt Spray Rating * 500 Hrs. mm creep. Q Panels	Hand-Cleaned CRS	Hand-Cleaned Hrs.
Controls:				
Corlar® Primer 825-8031/VG-88339	848-E-89-1	2,1	4,B	4.5, SB
Dulux® Primer 67-746	848-E-93-3	1,1	4	3
RC-65851/RC-H-40981 (Clear Corlar®)	848-E-93-1R	10,10	2.5,B	3
RC-60462/H-253 (Clear Dulux®)	848-E-101	CF	CF	CF
Inorganic Zinc 347-931	Zinc-Rich	0		
Experimental Candidates:				
1. Epon 826/Shell Ketimine H-3	848-E-89-2	2,1	1.5,B	2
2. Epon 826/Ketimine H-3/Kencure C_9P	848-E-89-3	1.5,B,2	3,B	1.5
3. Epon 826/Ketimine H-3/Dion 3800	848-E-89-4	1.5,1.5	1,B	2
4. Epon 826/Experimental Ketimine/ Dion 3800	848-E-89-6	2,1	2.5,B	3
5. Epon 826/Araldite 830-850	848-E-89-8R	2.5,3	2,B	3
6. Epon 826/Araldite 830-850/CE	848-E-89-9	3,3	2,B	3
7. Epon 826/Araldite 830-850/CE	848-E-89-10	3.5,5	2,B	2.5
8. Epon 826/Araldite 830-850/CE	848-E-89-11R	5,5	2,B	1,SB,2
9. Epon 1001/Ketimine 786-E-80	848-E-100-3	2,SB,1	1.5,SB	1.5,SB
10. Epon 1001/Ketimine 848-E-97	848-E-100-6	2,SB,1	1.5,SB	1.5,SB
11. Epon 826/Versamide 280B75	848-E-98-5	2,1	2	1.5
12. Epon 826/Emerez 1514	848-E-90-1R	3,5	2.5,B	2
13. Epon 826/Emerez 1514/Dion 3800	848-E-90-2R	5,1	2.5,SB	2.5
14. Epon 826/Emerez 1514/SACI-700	848-E-93-4	4,1	2.5	3
15. Desmodur E-21	848-E-90-3	2,B,1	2,B	2,B,3

Revised 12/27/76

*First Number for Clear Primer, Second Number for Topcoated Primer

PRIMER DEVELOPMENT FOR MAINTENANCE FINISHES

2 mil DFT Primer + 2 mil DFT Topcoat 369-Y-67641

System Description	Type	Initial	Mixing	% Solids (Wt.)
Controls:				
Corlar® Primer 825-8031/VG-88339	Epoxy/Polamide	210		
Dulux® Primer 67-746	Alkyd-Air Dry	150		
RC-65851/RC-H-40981	Corlar® Clear	30		
RC-60462/H-253	Dulux® Clear	90		
Inorganic Zinc Ganicin®	Zinc Rich Inorganic			
Experimental Candidates:				
1. Epon 826/Shell Ketimine H-3	Epoxy/Ketimine	100	120	90
2. Epon 826/Ketimine H-3/Kencure C_9P	Accelerated Epoxy/Ketimine	40	60	80
3. Epon 826/Ketimine H-3/Dion 3800	Accelerated Epoxy/Ketimine	40	100	80
4. Epon 826/Experimental Ketimine/ Dion 3800	Accelerated Epoxy/Ketimine	30	70	80
5. Epon 826/Araldite 830-850	Epoxy/Modified Aromatic Amine	60	450	75
6. Epon 826/Araldite 830-850/CE	Epoxy/Modified Aromatic Amine	60	150	80
7. Epon 826/Araldite 830-850/CE	Epoxy/Modified Aromatic Amine	60	150	80
8. Epon 826/Araldite 830-850/CE	Epoxy/Modified Aromatic Amine	80	475	80
9. Epon 1001/Ketimine 786-E-80	Epoxy/Ketimine	40	60	55
10. Epon 1001/Ketimine 848-E-97	Epoxy/Ketimine	40	60	52
11. Epon 826/Versamide 280B75	Epoxy/Polyamide	30		50
12. Epon 826/Emerez 1514	Epoxy/Polyamide	60	250	70
13. Epon 826/Emerez 1514/Dion 3800	Epoxy/Polyamide, Accelerated	100	400	70
14. Epon 826/Emerez 1514/SACI-700	Epoxy/Polaymide/Basic Sulfonate			50
15. Desmodur E-21	Moisture Cure Isocyanate	60	--	65

Revised 12/27/76

APPENDIX IIIB

cc: T. J. Coletti, Mar. Lab (2)
R. W. Laurrell, Mar. Lab
M. P. Morse, Mar. Lab
J. P. Huff, Mar. Lab
W. Pregmon, Mar. Lab
J. R. Courtright, Mar. Lab
R. L. Davis, Beaumont
R. D. Phelps, Troy Lab
P. W. Britt, Southfield
E. J. Zinser, Wilmington
A. G. Armour, Exp. Sta.
P. H. Pettit, Jr., Exp. Sta.
C. A. Senkler, Exp. Sta.
File, Exp. Sta.

EXPERIMENTAL STATION LABORATORY EXPOSURE NO. 24216

DATE: March 31, 1977

TITLE: EXPERIMENTAL HIGH SOLIDS PRIMERS

PURPOSE:

Obtain general durability of high solids primers over hand-cleaned rusty steel and compare with Corlar® and Dulux® primers.

MATERIAL EXPOSED: Topcoat 369-Y-67641, 2 mil DFT

Primers		Code*
Controls		
67-746	Dulux®	6-1, C-CRS
825-8031/VG-88339	Corlar®	6-2, C-CRS
347-Y-931	Ganicin®	6-3, SB-HRS
EXPERIMENTAL CANDIDATES		
848-E-135-3A	Epoxy/Ketimine	6-4, C-CRS, R-CRS, R-HRS
848-E-135-3B	" "	6-5, C-CRS, R-CRS, R-HRS
848-E-135-3C	" "	6-6, C-CRS, R-CRS, R-HRS
848-E-137	Epoxy/Polyamide	6-7, C-CRS, R-CRS, R-HRS
848-E-138	Epxoy/Amine	6-8, C-CRS, R-CRS, R-HRS
848-E-139	Epoxy/Polyamide	6-9, C-CRS, R-CRS, R-HRS
848-E-141	Epoxy/Amine	6-10, C-CRS, R-CRS, R-HRS
848-E-93-3	Dulux® 67-746	6-11, C-CRS, R-CRS, R-HRS
848-E-89-1	Corlar® 825-8031/ VG-88339	6-12, C-CRS, R-CRS, R-HRS
848-E-142	Ganicin® 347-Y-931	6-13, C-CRS, R-HRS
848-E-144	Epoxy/Ketimine, 30% PVC	6-14, C-CRS, R-CRS, R-HRS
848-E-143**	Epoxy/Ketimine Al filled	6-15, C-CRS, R-CRS, R-HRS

PANEL PREPARATION:

Rusted hot rolled steel panels were hand cleaned by 5 strokes with wire brush at each area in one direction.

All primers and topcoats were applied by air-spray to 4 mil DFT on primer and 2 mil DFT on topcoat. Primers were air-dried at least overnight before topcoats were applied. All panels were air-dried at least 2 weeks before exposure.

Ganicin® primer over sand blast cleaned hot rolled steel was supplied by W. Pregmon, Marshall Laboratory.

- over -

EXPOSURE INSTRUCTIONS:

One set each of these panels would be exposed indefinitely:

1. Beaumont, Texas, Test Racks; return after every 6 months.
2. Florida 45°S; return after every 6 months.
3. Salt Spray Cabinet.

REFERENCE:

Notebook 878-E

CHARGE CODE:

7354-211515-1400

---

*C-CRS - Polished clean cold rolled steel - Parker panels
R-CRS - Hand-cleaned rusted cold rolled steel, Delaware exposed
R-HRS - Hand-cleaned rusted hot rolled steel, Delaware exposed

**Remade as 878-E-42 and included in Exposure Series No. 24217 because of rough surface.

R. T. KHANNA

RTK:ayk
3/31/77

cc: T. J. Coletti, Mar. Lab (2)
R. W. Laurrell, Mar. Lab
M. P. Morse, Mar. Lab
J. P. Huff, Mar. Lab
W. Pregmon, Mar. Lab
J. R. Courtright, Mar. Lab
J. B. Emmons, Beaumont-TX
R. D. Phelps, Troy Lab
P. W. Britt, Southfield
E. J. Zinser, Wilmington
D. Metzger, Wilmington
P. H. Pettit, Jr., Exp. Sta.
B. V. Gregorovich, Exp. Sta.
C. A. Senkler, Exp. Sta.
File, Exp. Sta.

EXPERIMENTAL STATION LABORATORY EXPOSURE SERIES NO. 24216

DATE: June 22, 1977

TITLE: EXPERIMENTAL HIGH SOLIDS PRIMERS - RESULTS OF 1500 HOURS SALT SPRAY CABINET

PURPOSE:

To obtain general durability of high solids primers over hand-cleaned rusty steel and compare with Corlar® and Dulux® primers.

RESULTS:

- Dulux® 67-746 on C-CRS (control, #6-1) and R-CRS and R-HRS (#6-11) shows dense blistering both in primer and topcoated section. The primer film is very weak and soft because of excessive water retention.
- Corlar® 825-8031/VG-88339 on C-CRS (control #6-2) performs excellent but fails on rusted panels (#6-12) by dense blistering and overall rusting.
- Low molecular weight polyamide Emerez 1514 cured epoxy primer (848-E-139, panel #6-9) failed by dense blsitering, probably because of inadequate cure or application.
- All other experimental candidates on rusted panels exhibited comparable performance to that of Corlar® 825-8031/VG-88339 on C-CRS.
- Following candidates with Talc and Micaceous Iron Oxide pigmentation were judged to be slightly superior to other experimental candidates:

  848-E-135-3C Epoxy/Ketimine Adduct (#6-6)

  848-E-141 Epoxy/Polyamine Adduct (#6-10)

  848-E-137 Epoxy/Polyamide Adduct (#6-7)

  These would be studied further.
- Ganicin® 347-Y-931 continued to show excellent performance on both SB-HRS and R-HRS.
- Aluminum flake filled Epoxy/Ketimine Adduct primer shows excellent performance.
- 20% PVC appears to be adequate for primers over rusty steel. A candidate (848-E-144, panel #6-14) pigmented at 30% PVC showed adhesion loss between primer and Imron® topcoat when exposed to salt spray.
- Experimental candidates are of low viscosity and have good wetting characteristics. This tends to saturate the rusty pores and greatly reduce water and oxygen transmission rates to the metal interface. Adhesion was judged to be excellent under both wet and dry conditions.

DISPOSITION:

The Salt Spray Cabinet panels have been retained by the writer.

R. T. KHANNA

RTK:ayk

SALT SPRAY RESULTS

SUBSTRATE: RUSTY HAND-CLEANED STEEL

PANEL NO.	1000 HOURS	1500 HOURS
6-1	PRIMER SOFT, BLISTERING →	
	TOPCOAT BLISTERING →	(CR) LARGE EDGE BLISTERS
6-2	PRIMER: EXCELLENT →	
	TOPCOAT: EXCELLENT →	
6-3	PRIMER: EXCELLENT →	
	TOPCOAT: SPOTTY RUST →	(R)*
6-4	PRIMER: EXCELLENT →	
	TOPCOAT: EXCELLENT →	
6-5	PRIMER: →	
	TOPCOAT: →	
6-6	PRIMER: →	
	TOPCOAT: →	
6-7	PRIMER: →	
	TOPCOAT: →	
6-8	PRIMER: →	
	TOPCOAT: →	
6-9	PRIMER: MEDIUM BLISTERS	MAX. BLISTERS (R)
	TOPCOAT: MEDIUM BLISTERS	MAX. BLISTERS (R)
6-10	PRIMER: EXCELLENT →	
	TOPCOAT: EXCELLENT →	
6-11	PRIMER: DENSE BLISTERS →	(R)
	TOPCOAT: DENSE BLISTERS →	
6-12	PRIMER: DENSE BLISTERS	BAD RUST, DENSE BLISTERS (R)
	TOPCOAT: DENSE BLISTERS	BLISTERED
6-13	PRIMER: EXCELLENT →	
	TOPCOAT: EXCELLENT →	
6-14	PRIMER: EXCELLENT →	
	TOPCOAT: EXCELLENT →	
6-15	PRIMER: EXCELLENT →	
	TOPCOAT: EXCELLENT →	

*R = REMOVED

EPOXY/POYAMINE PRIMER
(878-E-88)

PART (A)

	INGREDIENTS Code	Names	G.W.	PARTS Flaked Epoxy	In-Situ Epoxy
I.	H-79	Cellosolve Acetate	8.06	82	12.3
II.	H-35	MEK	6.66	22	82.0
III.	KG-1105	Epon 1001	10.05	25	
IV.	RC-H-40984	In-Situ Epoxy (72% S)	8.81		34.72
V.	W-109	Talc	22.51	51.4	51.4
VI.	316-MiOx	MiOx	39.0	85.2	85.2
VII.	G-1109	Epon 826	9.7	75.0	75.0
VIII.		Cardura E	8.05	9.4	9.4
	TOTAL			350.0	350.0

Gal. Wt. = 12.07 ⟶ 11.24

R.M. Cost, $/gallon = 5.45 ⟶ 4.65

Viscosity = 4.2-400 poise, T.I. = 95

% Solids = 70.3 (wt.), 54.05 (volume)

PART (B)

	INGREDIENTS Code	Name	G.W.	
I.	H-79	Cellosolve Acetate	8.06	8
II.	H-35	MEK	6.66	17
		Araldite 830	9.3	28
		Araldite 850	9.4	28
	TOTAL			81

Gal. Wt. = 8.63

Raw Material Cost, $/gallon = 8.41

Viscosity = 20-70 cps

% Solids = 69 (wt.), 62.8 (vol.)

FORMULATED PRIMER

Mix Ratio = 4.32 by weight, 3.1 by volume

% Solids = 70 (weight)
= 56 (volume)

Gal. Wt. = 11.4 R.M. Cost $/gallon = 6.20

Coverage = 900 sq. ft./mil gallon

Viscosity = 1.1-16 poise, T.I. = 15

APPLICATION CHARACTERISTICS

Pot Life = 10 hours+

Dry Time ∿3 hours, cure overnight+

Film Build/Coat = 3 mil WFT on smooth surfaces
= 6 mil WFT on rusty surfaces

Coats/6 mil DFT = 4

SPRAY VERY WET FIRST COAT, FLASH ½-1 HOUR AND RECOAT TO DESIRED DFT.

DRY BULB TEMPERATURE = 76°F

% R.H. = 43%

RTK:ayk (6/9/77)

EPOXY/POLYAMIDE PRIMER
(878-E-90)

PART (A)

	INGREDIENTS			PARTS
	Code	Name	G.W.	(Weight)
I.	H-49	Toluene	7.18	41.2
II.	H-12	Butanol	6.72	40.0
III.		Versamid 280BX75	8.0	56.0
IV.		Genamid 2000	8.15	4.0
V.	W-109	Talc	22.51	47.2
VI.	316-MiOx	MiOx	39.0	76.6
	TOTAL			265.0

Gal. Wt. = 11.5
R.M. Cost, $/gallon = 5.00
Viscosity = 3-64 poise, T.I. = 20
% Solids = 64% wt., 44% vol.

PART (B)

	INGREDIENTS			PARTS
	Code	Name	G.W.	(Weight)
I.	G-1109	Epon 826	9.7	100.0
II.	H-49	Toluene	7.18	11
III.	H-12	Butanol	6.72	10
	TOTAL			121

Gal. Wt. = 9.1
R.M. Cost, $/gallon = 5.90
Viscosity = 112-146 cps, T.I. = 1.3
% Solids = 83% weight, 77.3% volume

FORMULATED PRIMER

Mix Ratios = 2.2 by weight, 1.74 by volume
Viscosity = 148-160 cps., T.I. = 1.1
Gal. Wt. = 10.6
PVC = 20%
R.M. Cost, $/gallon = 5.35
Coverage = 900 sq. ft./gallon mil
R.M. Cost ¢/ft.^{2} mil = 0.6
% Solids = 70% weight, 56% volume

APPLICATION CHARACTERISTICS

Pot Life = 4 hours+
Dry Time = 3 hours, overnight cure
Film Build/Coat = 6 mil WFT on clean smooth surfaces
= 8 mil WFT on rusty surfaces
Coats/6 mil DFT = 2

SPRAY VERY WET FIRST COAT, FLASH ½-1 HOUR, APPLY SECOND AND THIRD COAT TO 6 MIL DFT

DRY BULB TEMPERATURE = 75°F

% R.H. = 54

RTK:ayk (6/9/77)

EPOXY/KETIMINE PRIMER
(878-E-85)

PART (A)

	INGREDIENTS			PARTS	
	Code	Names	G.W.	878-E-85 Flaked Epoxy	In-Situ Epoxy
I.	H-79	Cellosolve Acetate	8.06	232	232
II.	H-35	MEK	6.66	132	93
III.	KG-1105	Epon 1001	10.05	100	
IV.	RC-H-40984	In-Situ Epoxy (72% S)	8.81		139
V.	W-109	Talc	22.51	192	192
VI.	316-MiOx	MiOx	39.0	312	312
VII.	G-1109	Epon 826	9.7	300	300
	TOTAL			1268	1268

Gal. Wt. = 12.15, R.M. cost, $/gallon = 5.25
T.I. = 100.0

Viscosity = 5-500 poise, % solids = 67% wt., 54.0% vol.

PART (B)

Epoxy curing agent Shell Ketimine H-3 = 184.0 parts

Gal. Wt. = 8.1

Viscosity = 2.7 poise

FORMULATED PRIMER

Mix Ratios	= 6.89 by weight, 4.6 by volume
Viscosity	= 1.9-60 poise, T.I. = 31
Gal. Wt.	= 11.555
PVC	= 20%
R.M. Cost $/gallon	= 6.65
Coverage $ft.^2$/mil-gal.	= 972
R.M. Cost ¢/$ft.^2$ mil	= 0.7
% Solids (wt.)	= 75
(vol.)	= 60.5
Pot Life	= 24 hours+

APPLICATION CHARACTERISTICS

Dry Time ~3 hours, cure overnight

Film Build/Coat = 7 mil WFT (3.5 mil DFT)

Coats/6 mil DFT = 2

SPRAY VERY WET FIRST COAT, FLASH ½-1 HOUR, APPLY SECOND COAT TO 6 MIL DFT

DRY BULB Temperature = 74°F

% R.H. = 50

RTK:ayk
6/9/77

EPOXY PRIMERS

For Hand-Cleaned Rusty Steel

	Epoxy/ Ketimine	Epoxy/ Polyamine	Epoxy/ Polyamide	Awlgrip 85A
% Solids (wt.)	75	70	70	54.4
(vol.)	60.5	56	56	40.3
Pot Life, Hours	24+	10+	4+	∞
PVC	20	20	20	19.4
R.M. Cost, $/gallon				
Wet	6.65	6.20	5.35	5.17
Dry	11.00	11.10	9.55	12.83
Gal. Wt., lbs./gallon	11.555	11.4	10.6	9.16
Dry Time, Hours	3	3	3	3
Wet Film Build	7	6	8	4
Coats/6 Mil Dry	2	2	2	3
Package	2	2	2	1
Unknowns/Problems	Cure latitude Penetration	Toxicity of residual amine Penetration	Penetration	Toxicity Film build

COST ESTIMATES

ZINC-FREE MAINTENANCE PRIMERS

	Gallon Weight	R.M. Cost $/Gallon	% Volume Solids	¢/Ft.^{2} Mil-Gal. (Dry)	R.M. Cost $/Dry Gallon
Controls					
Corlar® 825-8031/ RC-H-40981	11.23	4.45 (10.87)*	40.6	0.7	11.00
Dulux® 67-Y-746	13.49	4.60	65.7	0.45	7.00
Experimental					
Epoxy/Ketimine Adduct	11.55	6.65	60	0.7	11.10
Epoxy/Polyamide	10.55	5.35	56	0.6	9.55
Epoxy/Polyamine Adduct	11.4	6.20	56	0.7	11.10
Epoxy/Ketimine Al Filler	9.8	11 → 8.46	56.5	1.2 → 0.93	19.50 → 15.00
Hypalon® - Clear	7.68	1.80	14.4	0.8	12.5
- Talc Filled	8.63	1.80	20.0	0.55	9.0
- MiOx Filled	8.58	2.33	17.65	0.8	13.2
- Aluminum Filled	8.26	4.00	17.1	1.5	23.40
Awlgrip 85A**	9.16	5.17	40.3	0.8	12.83

*Mill cost. Note high conversion costs.

**Recommended spray solids ∿30% (vol.) solids

RTK:ayk
Revised 6/15/77

cc: T. J. Coletti, Mar. Lab (2)
R. W. Laurrell, Mar. Lab
M. P. Morse, Mar. Lab
J. P. Huff, Mar. Lab
W. Pregmon, Mar. Lab
J. R. Courtright, Mar. Lab
R. L. Davis, Beaumont
R. D. Phelps, Troy Lab
P. W. Britt, Southfield
E. J. Zinser, Wilmington
A. G. Armour, Exp. Sta.
P. H. Pettit, Jr., Exp. Sta.
C. A. Senkler, Exp. Sta.
File, Exp. Sta.

EXPERIMENTAL STATION LABORATORY EXPOSURE NO. 24217

DATE: March 31, 1977

TITLE: EXPERIMENTAL PRIMERS FOR RUSTY STEEL

PURPOSE:

Obtain general durability of high solids primers over hand-cleaned rusty steel and compare with Ganicin® IOZ primer.

MATERIAL EXPOSED: Topcoat 369-Y-67641, 2 mil DFT

Primer			Code*
848-E-147-A	Epoxy/Ketimine	Zn-Flake	7-1, C-CRS, R-HRS
848-E-147-B	"	Ser-X	7-2, C-CRS, R-HRS
848-E-147-C	"	W-88	7-3, C-CRS, R-HRS
848-E-147-D	"	Glass Flake	7-4, C-CRS, R-HRS
848-E-147-E	"	Zn-Flake	7-5, C-CRS, R-HRS
878-E-38-1	Hybrid with W-198		7-6, C-CRS, R-HRS
878-E-38-2	Hybrid with Zn-Flake		7-7, C-CRS, R-HRS
848-E-147-F	Epoxy/Ketimine	W-198	7-8, C-CRS, R-HRS
878-E-42	Epoxy/Ketimine	W-128	7-9, C-CRS, R-HRS
Control			
347-Y-931			7-10, SB-HRS

PANEL PREPARATION:

Rusted hot rolled steel panels were hand cleaned by 5 strokes with wire brush at each area in one direction.

All primers and topcoats were applied by air-spray to 4 mil DFT on primer and 2 mil DFT on topcoat. Primers were air-dried at least overnight before topcoats were applied. All panels were air-dried at least 2 weeks before exposure.

Ganicin® primer over sand blast cleaned hot rolled steel (control) was supplied by W. Pregmon, Marshall Laboratory.

EXPOSURE INSTRUCTIONS:

One set each of these panels would be exposed indefinitely:

- over -

1. Beaumont, Texas, Test Racks; return after every 6 months.
2. Salt Spray Cabinet.
3. Florida 45°S Test Racks; return after every 6 months.

REFERENCE:

Notebook 878-E

CHARGE CODE:

7354-211515-1400

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*C-CRS - Polished clean cold rolled steel - Parker panels
R-CRS - Hand-cleaned rusted cold rolled steel, Delaware exposed
R-HRS - Hand-cleaned rusted hot rolled steel, Delaware exposed

R. T. KHANNA

RTK:ayk
3/31/77

FLAKE PIGMENTS

Zinc Flake 21 HF (at 88% wt. solids)

Ser-X Talc platelets

Wet Ground Mica (W-88)

Glass Flake (1/64" Hammered Flake)

Aluminum Flake (W-128)

COST ESTIMATES

ZINC-RICH MAINTENANCE PRIMERS

	Gallon Weight	R.M. Cost $/Gallon	% Volume Solids	R.M. Cost $/Dry Gallon	¢/Ft.^{2} Mil-Gal. (Dry)
Control					
Ganicin® 347-Y-931	21.75	11.54(14.48)*	42.8	27.0	1.7→1.3
Experimental					
Zn Dust Primer 878-E-43	25.7	14.0	72	19.50	1.2
Zn Flake Primer 848-E-147-A	13.1	11.55	59	19.60	1.2

*Mill cost. Note that R.M. Cost is strongly influenced by the price of zinc.

RTK:ayk

Revised 6/15/77

APPENDIX IIID

cc: T. J. Coletti, Mar. Lab (2)
R. W. Laurrell, Mar. Lab
M. P. Morse, Mar. Lab
J. P. Huff, Mar. Lab
W. Pregmon, Mar. Lab
J. R. Courtright, Mar. Lab
J. B. Emmons, Beaumont
J. M. Donatello, Exp. Sta.
File, Exp. Sta.
R. D. Phelps, Troy Lab
P. W. Britt, Southfield
E. J. Zinser, Wilmington
D. W. Metzger, Wynnewood
A. G. Armour, Mechelen
P. H. Pettit, Jr., Exp. Sta.
B. V. Gregorovich, Exp. Sta.
C. A. Senkler, Exp. Sta.

EXPERIMENTAL STATION LABORATORY EXPOSURE NO. 24323

DATE: October 7, 1977

TITLE: Experimental High Solids Primers

PURPOSE:

Obtain general durability of high solids primers over hand-cleaned rusty steel and compare with controls.

MATERIAL EXPOSED:

Topcoat 369-Y-67641, 2 mil DFT

Controls (see attached)

PANEL PREPARATION:

Rusted hot rolled steel panels were hand-cleaned by five strokes with wire brush at each area in one direction. Primers were air-dried at least overnight before topcoats were applied. All panels were air-dried at least two weeks before exposure.

Ganicin® primer over sandblast cleaned hot rolled steel and hand-cleaned rusty hot rolled steel was supplied by W. Pregmon, Marshall Laboratory.

EXPOSURE INSTRUCTIONS:

One set each of these panels would be exposed indefinitely:

1. Beaumont, Texas, Test Racks; return after every 6 months.
2. Chambers Work
3. Salt spray cabinet at Experimental Station

REFERENCE:

Notebook 878-E

CHARGE CODE:

7354-211515-1400

R. T. KHANNA

RTK:adw
Attach.

Controls: Series #	Description And Substrates	Application	Film Thickness (Primer) mils
24323-1	347-931 Ganicin® SB-HRS	Sprayed	3
-2	347-931 Ganicin® HC-HRS	Sprayed	3
-3	67-746 Dulux® HC-HRS	Brushed	4
-4	67-H-43034 Dulux® HC-HRS	Brushed	4
-5	Awlgrip 85A HC-HRS	Sprayed	2
-6	HC-HRS	Sprayed	2
-7	SB-HRS	Sprayed	2
-8	825-8031/VG88339 Corlar® SB-HRS	Sprayed	4
Experimental Candidates			
24323-9	TMPTMA (50%) modified Dulux® 67-746 HC-HRS	Brushed	4
-10	TMPTMA (50%) modified Dulux® 67-H-43034 HC-HRS	Brushed	3
-11	TMPTMA (30% of vehicle) modified Dulux® 67-H-43034 HC-HRS	Brushed	4
-12	" HC-HRS	Sprayed	3
-13	" SB-HRS	Sprayed	3
-14	Epoxy/ketimine W-178 pigmentation HC-HRS	Sprayed	4
-15	Epoxy/ketimine zinc flake pigmentation HC-HRS	Sprayed	3
-16	" SB-HRS	Sprayed	3
-17	Epoxy/ketimine Zinc molybdate pigmentation HC-HRS	Brushed	4
-18	" HC-HRS	Sprayed	4
-19	Epoxy/ketimine W-178 with Sicorin RZ HC-HRS	Sprayed	5-6
-20	Epoxy/ketimine W-178 with Arazate® HC-HRS	Brushed	5-6
-21	Epoxy/phenalkamine W-178 pigmentation HC-HRS	Brushed	4-5
-22	Epoxy/Versamid W-178 pigmentation HC-HRS	Brushed	5-6
-23	Alkyd/acrylate/urethane (70%+ vol. solids)primer HC-HRS	Brushed	3

RTK:adw
10/7/77

APPENDIX IV

CORROSION CONTROL BY INHIBITORS IN COATINGS

REK Nov 8,1976

PRIMER FOR RUSTY STEEL

LITERATURE SURVEY

- CORROSION MECHANISM AND ITS PREVENTION
- ROLE OF INHIBITORS IN CORROSION CONTROL
- USE OF INHIBITORS AND LEADS FOR THEIR USE IN PRIMER SYSTEMS

CONCLUSIONS

- ORGANIC VEHICLES ALONE PROVIDE LIMITED PROTECTION

  HIGH PERMEATION OF O_2, WATER, AND IONS IN ALL ORGANIC FILMS BECAUSE OF MOLECULAR INTERACTIONS, SOLUBILITY, AND VOIDS
- EXCESSIVE WATER IS ALWAYS PRESENT AT THE INTERFACE AND WATER CAUSES ADHESION LOSS AS A PREREQUISITE FOR THE START OF CORROSION PROCESS
- OXYGEN PERMEATION IS THE SLOWEST PROCESS AND CONTROLS THE CORROSION RATE
- ELECTROLYTIC CELLS ARE BUILT-IN STEEL
- BEST PRIMER VEHICLES (LOW PERMEABILITY) ARE THOSE BASED ON AROMATIC/INORGANIC OR HYBRID SYSTEMS
- SUPPLEMENT WITH INHIBITORS, EVEN POORER VEHICLES MAY PROVIDE ADEQUATE PROTECTION
- MAINTAIN NEUTRAL/ALKALINE ENVIRONMENT AT INTERFACE

ALTERNATIVES FOR PRIMER DEVELOPMENT

- PROVIDE IN-SITU CURE PENETRANT
- PROVIDE CORROSION IMMUNITY BY INHIBITORS
- BUILD-IN LEACHABLE PASSIVATING IONS IN THE COATING AS A CONTROL OF THE ENVIRONMENT AT THE INTERFACE
- PROVIDE VERY HYDROPHOBIC PRIMER WITH OPTIMUM WET ADHESION → MAINTAIN ADHESION AND UTILIZE INTERFACE WATER TO PLASTICIZE VEHICLE; A NON-INTERACTING POLYMER WOULD LOSE ADHESION
- BUILD-IN HIGH BUFFERING CAPACITY TO RETAIN ALKALINITY
- PROVIDE PRIMER WITH LOWEST PERMEABILITY PROPERTIES, ESPECIALLY O_2 PERMEABILITY
- MAINTAIN BASIC MEDIA AT THE INTERFACE
- PROVIDE COMPLEXES THAT RESULT IN INSOLUBLE, INPERMEABLE IRON COMPOUNDS; PHOSPHATES, BORATES
- INCREASE TORTUOSITY WITH "TREATED FILLER" OF MAXIMUM PLATELET CONFIGURATION, MICA, Zn, Al
- PROVIDE SACRIFICIAL PROTECTION BY ELECTROCHEMICAL MEANS, Zn, Al, Mg, SALTS/DUST
- USE MULTI- VALENT COMPOUNDS TO FORM INORGANIC POLYMERS WITH Ca, Ba, Zn, SULFONATES, FORMATES, OXALATES, PROPIONATES, PALMITATES, SEBACATES, AND AZEALATES
- INHIBITING PIGMENTS/INHIBITORS ADDED EXTERNALLY
- HIGH ELECTRICAL RESISTIVITY VEHICLE

MODES OF CORROSION CONTROL

A. PHYSICAL BARRIER (PERMEABILITY)
   - VEHICLE (ORGANIC VERSUS INORGANIC)
   - FILLER (PARTICLE SIZE, PLATELETS)
   - THICKNESS (MICRONS TO MILLIMETERS)

B. CHEMICAL BARRIER (PASSIVATION, INHIBITION)
   - CHROMATES
   - BUFFERS
   - ADSORBING AMINES, ETC.

C. ELECTROCHEMICAL BARRIER (SACRIFICIAL Zn, Mg)

D. ELECTRICAL BARRIER (CATHODIC PROTECTION)

EXAMPLES:

1. ORGANIC PAINTS (A + B)

2. INORGANIC ZINC (A + C)

3. DRILLING FLUID, PROCESS WATER (B + OXYGEN SCAVENGERS)

4. METAL PRETREATMENT (INORGANIC COATINGS)

CRITERIA FOR CORROSION INHIBITORS

- VERY SLIGHT SOLUBILITY IN WATER
  - Enough to maintain and replenish inhibitor at the interface
- INSOLUBLE PRODUCTS OF REACTION with iron, vehicle, or water
- ABILITY TO FORM COMPLEXES - Inorganic polymeric films of very low permeability (high crystallinity)
- HIGH BUFFERING CAPACITY - Enough to maintain near neutral or alkaline (pH $\geq$ 7) at all times under acidic exposures for the text interval, 1000-2000 hours/salt spray
- Multiple reactant yielding by-products which are more effective inhibitors

  Isocyanates → Amines → Carbamates

LIST OF POTENTIAL CORROSION INHIBITORS

1. Zn, Ba salts of nitro/amino/phenolic-ACIDS
2. Zn, Ba complex of polyamines and boric acid
3. Aromatic amine salts of nitrites, stearates, azealates, benzoates, phosphates
4. Ba stearates, benzoates, fluoride, feldspar (AlF_3), fluorospar (CaF_2), Ba fluorosilicate, Zn acetylacetonate
5. $NH\langle^{(CH_2)_nCooBa}_{(CH_2)_nCooBa}$
6. a. 2,4 Dinitro, O-nitro-aniline
   b. p-Amino diethyl aniline
7. Di-phenyl amine $NH\langle^{\phi}_{\phi}$, O-nitro-derivatives
8. Di-phenyl acetonitrile
9. N,N'-diphenylurea (carbanilide)
10. N,N'-diphenyl guanadine
11. N,N'-diphenyl benzoguanamine
12. Substituted propyl amine (Jefferson), piperazine
13. N,N'-diethylcyclohexylamine
14. N,N'-cyclohexylamine carbamate
15. Substituted Dicy, melamine
16. p-Nitro,-O-amino phenols
17. O-nitro benzonitriles
18. Amino pyridines
19. p-Amino benzene sulfonamides
20. O-Toluidine
    O-Anisidine
    O-Phenetidine
    MPDA
    MDA derivative
    Amino-benzoic acids
    Amino-phenols

21. Sodium hexametaphsophate (MPPG) glass containing Ba, Zn, Ca, Mg, Al oxides, phosphates, promoting "scale formation" such as $FeCa(PO_3)_s 8H_2O$

22. Fatty acid derivatives $R \sim C_{18}H_{37}$

a) 1°, 2°, 3° amine

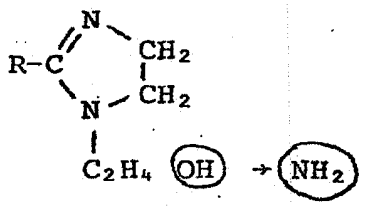
b) Diamine

c) Amides $R-N\begin{matrix}(CH_2CH_2O)_xH \\ (CH_2CH_2O)_yH\end{matrix}$

d) Salts of above with oleic, dimer, naphthenic, phosphonic, benzoic acids

e) Amphoterics $CH_3-\underset{\underset{R-NH}{|}}{CH}-CH_2COOH$

f) Morpholines, imidazolines, derivatives, and salts



23. 1,2-Hydroxyethyl-1-benzyl-2-tridecyl-2-imidozolium nitrite, benzoate, azelate

24. Pyridine monocarboxylic, picolinic, 180°-nicotinic acids and their basic salts

25. Benzotriazole

2,4,6-collidine (0.1M optimum concentration)

2,6-lutidine 0.1M

pyridine 0.15M

26. $NO_2\ \phi\ NH_2 \cdot H_3BO_3 \cdot BaO$

$3[NO_2\ \phi\ NH_2]H_3BO_3$

$NO_2\ \phi\ NH_2 \cdot H_3BO_3 \cdot ZnO$

$NO_2\ \phi\ NH_2 \cdot COOH-CH_2)_7 CooBa$

$NO_2\ \phi\ NH_2 \cdot OPA \cdot \frac{1}{2}BaO$ (or $\frac{1}{2}ZnO$)

27. Polymeric

a) (Epon 826)$\cdot H_3PO_4 \cdot$ BaO(ZnO)
$\cdot$Fatty amine
(Aromatic amine/DETA/TETA)$\cdot H_3PO_4 \cdot (H_3BO_3)$

b) (Sty/MA_n)-Zn, Ba Salt

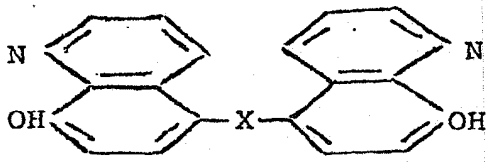
c) (Polyamic acids) Zn Ba salts

d) P(MMA/MAA) copolymers, complex polyamines BaO, ZnO

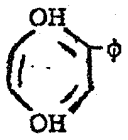
e) p(MA)→hydroxylamine $\underset{\underset{NH-OH}{|}}{C=O}$ (hydroxyamic acid)

28. Above materials prepared as encapsulated pigment

29. Compounds that form stable coordination complex with iron, zinc, Mg, Al, Ba



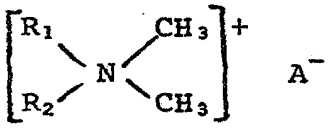
Hydroquinone bischelate
Ferrocene - cyclopentadiene complexes



30. Boron nitrite

31. Mercaptobenzotriazole Na, Ba, Zn salts

32. Quaternaries



33. Fluoro-alumino-silicate glasses

Ion-leachable glasses

Fluorobonic acids

Quartz + Al_2O_3 + Flux of Na, Ca, AlF_3 $Al(PO_4)_2$ at 1050-1350°C for 40-150 minutes

Ba borosilicate, Ba metaborates

Zn hexafluorosilicate, Zn borate

34. 2,4-Dinitrophenol-MDI/TDI. Polyamino-acid. (ZnO/BaO)

RTK:ayk
10/28/76

CR & D DEPARTMENT HELP REQUESTED IN THE FOLLOWING AREAS:

1. SELECTION/DESIGN - SYNTHESIS OF INHIBITORS
   - AMINES OF ADEQUATE SOLUBILITY/EFFECTIVENESS BALANCE
   - COMPLEXING AGENTS CAPABLE OF FORMING INSOLUBLE INORGANIC SCALE AT THE INTERFACE
   - ZINC, CALCIUM COMPOUNDS, ORGANOMETALLIC COMPLEXES THAT MAY PARTICIPATE IN CORROSION PROCESS

2. INORGANIC COATINGS - AIR DRY
   - INSOLUBLE
   - BOND TO IRON/RUST

   SILICATE, TITANATE, BORATES, AND OTHER METAL OXIDES

3. CORROSION SCIENCE AND CHEMICAL MEANS OF CORROSION CONTROL - PRIMARY INTEREST IN SALT-WATER INDUCED CORROSION

CORROSION AND INHIBITORS

SELECTED PUBLICATIONS

1. CORROSION, VOL. I & II, SHRIER
2. CORROSION INHIBITORS, NACE
3. CORROSION INHIBITORS, BREGMAN
4. CORROSION INHIBITORS, MANUFACTURE, AND TECHNOLOGY - RANNEY (NOYES DATA)
5. CORROSION AND CORROSION CONTROL, UNLIG
6. BETZ HANDBOOK OF INDUSTRIAL WATER CONDITIONING
7. EUROPEAN SYMPOSIUM ON CORROSION INHIBITORS

LIST OF COMMERCIALLY AVAILABLE CORROSION INHIBITING NON-CHROMATE PIGMENTS AND INHIBITORS

Name

Zinc Oxide (W-8)
Zinc Phosphate '317'
Zinc Molybdate (molywhite 101)
(molywhite 212)
Zinc Phosphooxide (Nalzin SC-1)
Zinc Flake 21 HF
Barium Metaborate (Busan 11 M1) (W-178)
Halox CW-2230 (Caclium Borosilicate) CW-22, CW-221
Halox CW-11, CW-111 (Calcium Phosphosilicate)
Zinc dibenzyldithiocarbamate (Arazate®)
Zinc Salt of Nitroisophthalic acid (Sicorin RZ)
Aluminum Flake (W-128)
Lithium Benzoate

CHROMATE AND LEAD-FREE ANTI-CORROSION PIGMENTS

As a result of recent legislative activity and the present atmosphere regarding use of "chromate" and "lead" containing pigments, many chemists in our technical organization are attempting to formulate anti-corrosion products with replacements for the tried and proven "red lead" and "zinc chromate" pigments.

This "C" addition to the monthly New Materials Report will be temporary in nature (4-6 months), but will attempt to provide the following information:

a. A listing of the various lead and chromate free pigments which are being offered or have been used in anti-corrosion products.

b. Identification of Chemists in the various laboratories who have received samples.

This will permit chemists to obtain background on results of previous experiments (if any were actually carried out), and may help prevent duplication of effort or waste of time if previous results were unpromising.

The Pigments listed below are those known (by the writer) at this time as being offered for this end use. If anyone knows of other pigments which should be added to the list, please drop a note to O. R. Volk, Marshall Laboratory, for inclusion in subsequent listings.

1. Moly-White® 101 - Zinc Molybdate compound manufactured by Sherwin-Williams Co. for use in solvent systems.

Samples received by: O. R. Volk, Mar. Lab.
E. J. Donnelly, Mar. Lab.
John Murray, Chicago Plant

2. Moly-White® 212 - Calcium Zinc Molybdate compound manufactured by Sherwin-Williams Co. for use in water dispersible and latex systems.

Samples received by: G. Goodell, Troy
O. R. Volk, Mar. Lab.
T. Smearing, Troy

3. Zinc Phosphate is available from Reichard-Coulston, Inc. as "317" Zinc Phosphate and from Mineral Pigments Corp. as "0852" Zinc Phosphate.

Samples received by: G. Goodell, Troy
J. A. Vasta, Mar. Lab.
M. M. Willey, Mar. Lab.
O. R. Volk, Mar. Lab.

4. "316" Micaceous Iron Oxide is available from Reichard-Coulston, Inc.

Samples received by: E. J. Donnelly, Mar. Lab.
O. R. Volk, Mar. Lab.

5. Halox® CW-11 is a calcium phospho silicate composite pigment available from Halox Pigs., a Division of Hammond Lead Prod., Inc. for use in water and oil systems.

Samples received by: E. J. Donnelly, Mar. Lab.
O. R. Volk, Mar. Lab.
E. R. Werner, Mar. Lab.

6. Halox® CW-111 is a fine particle size grade of CW-11.

Samples received by: E. J. Donnelly, Mar. Lab.

7. Halox® CW-22 is a calcium boro silicate composite pigment available from Halox® Pigs., a Division of Hammond Lead Prod., Inc. for use in water and oil systems.

Samples received by: O. R. Volk, Mar. Lab.
E. J. Donnelly, Mar. Lab.
E. R. Werner, Mar. Lab.
J. Jeffery, Flint

8. Halox® CW-221 is a fine particle size grade of CW-22.

Samples received by: O. R. Volk, Mar. Lab.
E. R. Werner, Mar. Lab.

9. Halox® CW-2230 is a calcium boro silicate composite pigment with a higher Boron content than CW-22.

Samples received by: O. R. Volk, Mar. Lab.
John Murray, Chicago Plant

10. Busan® 11-M-1 silica modified barium metaborate pigment, is available from Buckman Laboratories, Inc., and can be used in water and oil systems.

Samples received by: Available for many years as Raw Material Code W-178.
John Murray, Chicago Plant

11. Zinc Oxide (W-41).

Samples evaluated by: John Murray, Chicago Plant

12. Sicorin® RZ is a zinc salt of an organic nitrogen compound for use in solvent and water based primers.

Samples received by: John Murray, Chicago Plant
T. J. Smearing, Troy Lab.

13. The April, 1976 issue of Journal of Coatings Technology contained a report from the New England Society for Coatings Technology Technical Committee comparing various Corrosion Inhibiting Pigments Used in Latex Coatings on Steel.

14. Paper No. 132, presented at the International Corrosion Forum in Houston, Texas, Mar. 22-26, 1976 described Rust Inhibitive Primers Utilizing Pigments Other Than Lead and Chromates.

15. Ferrophos® Pigment is Fe_2P and is used in zinc rich coatings as a replacement for Zn metal. It provides improvements in weldability, gas torch cutting efficiency, intercoat adhesion and economics.

Samples received by: M. M. Willey, Mar. Lab.
J. R. Courtright, Mar. Lab.

Polidura has found Molywhite 101 to work well in oil/solvent systems but that Molywhite 212 and Sicorin RZ did not perform satisfactorily in water based systems. If other researchers would like to share their results (reports) on work with the above anti-corrosion materials, please contact Chris Peters, Room B-1244, Brandywine Bldg., Wilm.

ORV:jp
7/15/76

NL Industrial Chemicals
NL Industries, Inc., Industrial Chemicals Division
P.O. Box 700 Hightstown, N.J. 08520 • 609/448-3200

NALZIN® SC-1

CORROSION INHIBITIVE PIGMENT

DS - 139

DESCRIPTION

NALZIN SC-1, a zinc phospho oxide complex, is a versatile lead free corrosion inhibiting pigment equally suitable for both aqueous & solvent based protective coatings.

TYPICAL PROPERTIES

Composition	Zinc phospho oxide complex
Form	Finely divided powder
Color	White
Density (gm/cm^3)	4.06
(lb/U.S. gal)	33.8
Bulking Value (U.S. gal/lb)	0.0296
Oil Absorption (gms/100 gms)	50 - 70
Bulk Density (gm/cm^3)	2 - 3
Solubility (in H_2O)	0.1% max

ADVANTAGES

- Stable in a wide variety of binder systems
- Highly efficient corrosion inhibiting action
- Suitable for virtually all types of coating systems
- White color allows formulating of virtually any color coating
- Minimizes tendency for flash rusting in aqueous coatings
- Excellent throwing power and can stability in electrodeposition coatings
- Excellent cost effectiveness

WHERE TO USE NALZIN SC-1

INDUSTRIAL and TRADE SALES anti-corrosive coatings

— over —

HOW TO USE NALZIN SC-1

SOLVENT BASED COATINGS:

Other than following proper formulating techniques, no special precautions need be taken.

We suggest anywhere from ¾ to 1½ lb NALZIN SC-1 per gallon. Studies indicate that in many cases loading in the ¾ to 1 lb range PERFORM as well as a 1½ lb/gallon loading.

Due to the relatively high oil absorption of NALZIN SC-1, it is suggested that loadings not exceed 2 lb/gal. Also, formula PVC should generally fall below 40%.

WATER BASED COATINGS:

Water Reducible: Same as solvent based coatings.

Latex Systems: NALZIN SC-1 works extremely well in all types of latex systems. For optimum performance we recommend:

1. Use ½ to 1 lb NALZIN SC-1 per gallon of coating.
2. Keep the pH of the coating within the desirable range for the polymer type:

   PVA's, vinyl/acrylics
   styrene/acrylics ..... pH: 8.5-9.5
   vinyl/ethylenes

   acrylics ..... pH: 9.0-10.0

3. Use sufficient dispersant and wetting agent to insure a stable system.
   - — Dispersants found to work well with NALZIN SC-1 include Rohm & Haas' "Tamol 850" as well as KTPP.
   - — We suggest about 1% dispersant (active) based on the total weight of the pigmentation as a start.
   - — Frequently a split dispersant addition (about ¾ in the grind, and ¼ in the letdown) works quite well.
4. Keep the PVC of the coating at 30% or less (due to the less than 100% binding efficiency of latices, the formula PVC must be kept well below the pigmentation CPVC to insure good film integrity).

Studies indicate that NALZIN SC-1 frequently performs as well at the ½ lb/gal level as at the 1 lb/gal level in latex systems.

The pH of the latex coating should be kept in the proper range for two reasons — one: dispersants are most effective at moderately high pH's and two: moderately high pH's are more conducive to freedom from corrosion (particularly flash rusting) while the latex coating is still wet.

LIST OF POTENTIAL INHIBITORS

(Suggested by Various Suppliers)

	Additive	Type
1.	Zelec® UN	C_{8-12} Phosphate
2.	Zelec® NK	C_{8-12} DEA Salt
3.	Zelec® UT	C_{16-18} Phosphate
4.	MPD-4577	Trithione
5.	MPD-4547	Titanate
6.	MPD-4548	OH-Titanate
7.	MPD-4546	Phosphate
8.	Ken-React TTOP-38	Phosphate
9.	Ken-React TTS	Titanate
10.	Ken-React TTOP-12	Phosphate
11.	Ken-React TTOPI-41B	Phosphite
12.	Ken-React GTDOP-138	Chelate Phosphate
13.	Ken-React GTDOP-112S	Chelate Phosphate
14.	Ken-React TTBS-9S	Sulfonate
15.	Ken-React TTBPP-58S	
16.	Armeen 2C	
17.	Armeen C	
18.	Armeen O	
19.	Duomeen T	
20.	Duomeen TDO	
21.	DMAMP-80/Pamolyn 300	
22.	DMP-30/Pamolyn 300	
23.	None	Control
24.	MPD-4549	Hydroxy-Titanate
25.	MPD-4629	Titanate
26.	MPD-4630	OH-Titanate
27.	MPD-4631	Titanate
28.	MPD-4632	OH-Titanate
29.	Pamolyn 300	
30.	WX-109	Pamolyn 220-Epoxy
31.	A-187	Epoxy-Silane
32.	DDBSA-OA	Amine-Salt

LIST OF POTENTIAL INHIBITORS

(Continued)

33.	DDBSA-OA 5% Solution	Amine Salt
34.	SACI-700	Ca Sulfonate of Petroleum
35.	Actan	Polyphenol Chelate
36.	Tectyl 506	
37.	Dicyclohexylamine ammonium nitrate	
38.	F-786	Epoxy-Silane
39.	Phenyl-Thio Urea	
40.	8-Hydroxy-Quinoline	
41.	Anthranilic acid	
42.	3,5-diaminobenzoic acid	
43.	p-nitroaniline	
44.	Surfynol 104	Acetylenic glycol
45.	2 EMI	
46.	Quinoline	
47.	m-Aminophenol	
48.	Nicotinic Acid	COOH
49.	Hexamethyleneimine	
50.	Lithium Benzoate, Cinnamate, Salicylate	
51.	Zinc dibenzyl thiocarbamate	
52.	Zinc imino diacetate	
53.	n-Butyl Stannoic Acid	
54.	n-Phenyl cyclohexylamine	

CORROSION CONTROL AND INHIBITOR TECHNOLOGY

- EVALUATE COMMERCIAL INHIBITORS IN ALKYD AND EPOXY VEHICLES
- EVALUATE PROTOTYPE INHIBITORS AND ESTABLISH TEST METHOD FOR INHIBITOR SCREENING
- ESTABLISH SELECTION CRITERIA FOR CORROSION INHIBITORS
- IDENTIFY MODE OF APPLICATION OF INHIBITORS
- DEVELOP HIGH ACTIVITY INHIBITORS AND ASSESS THEIR USEFULNESS IN FINISHES
- IDENTIFY OTHER POTENTIALLY FEASIBLE APPLICATIONS OF INHIBITORS; METAL TREATMENT, WASHCOATS, ETC.

APPENDIX V

QUICK-SET CURE PENETRANT PRIMER

RESULTS

1500+ HOURS SALT SPRAY OF HYPALON® BASED IN-SITU CURE PRIMER

- Penetrant III
  Accelerator 808/BMA/XD-9002//10/60/30
  and Penetrant V
  Accelerator 808/XD-9002//10/90
  at 20% solids in xylene, H-79, or MIBK are preferred candidates

- W-128 aluminum based primer performs extremely well over R-HRS

- Aluminum powder filled primers are too permeable and fail by spot rusting

- Performance on C-CRS (Q-panel polished) was consistently inferior in the entire series

Recommendations:

1. Assess toxicity of Accelerator 808®
2. Determine if low solids system is a viable candidate
3. Confirm safety aspects of handling aluminum flake with Hypalon®
4. Consider alternate low/no toxicity systems

RTK:ayk
6/17/77

E. I. DU PONT DE NEMOURS AND COMPANY
Fabrics and Finishes Department

FFD No.: _____

Date: 4/12/77

TO: J. E. GRIFFITHS, LEGAL, WILMINGTON

FROM: R. T. KHANNA, F & F, EXPERIMENTAL STATION

REQUEST TO FILE A PATENT APPLICATION

Descriptive Title:

FINISHES FOR RUSTY STEEL AND OTHER MARGINALLY CLEAN SURFACES

Summary of Invention:

A coating system characterized by the following:

(a) Penetrant and/or good surface wetting agents capable of undergoing in-situ cure to a coherent film when coated with a suitable topcoat. The penetrant can be a single component or a blend of reactive components. It is of low viscosity and possesses good penetration and surface wetting properties. Viscosity can be further reduced by dilution with a medium volatility solvent.

(b) A primer containing a reactive species [as a part of the backbone or an external additive(s)] which on contact with the chemical species of the penetrants initiates cure of the underlying film and provides interfacial grafting and/or crosslinking with the constituents of the penetrants; preferably it is pigmented.

(CONTINUED ON ATTACHED PAGE)

Publications:

This is an extension of Du Pont's effort in "Quick-Set Acrylic Adhesives" (Cavalon®) with the difference that, for the purpose of present application, Hypalon 30 is dissolved in a hydrocarbon solvent instead of a reactive monomer (MMA, BMA, etc.). The use of monomer to dissolve is not excluded but is restricted here to eliminate (a) toxicity, (b) volatility and odor, and (c) air-inhibition of the cure at the air-polymer interface. Monomers and/or additives that overcome these problems can be used in the practice of this coating system.

Detailed references can be obtained from our Cavalon® acrylic adhesive program.

Importance of Invention:

Coating rusty steel without elaborate cleaning such as sand blasting, abrasive grinding, polishing, and/or careful metal treatments (chromate or phosphate) has been an unattainable goal for a long time. This is an initial effort to identify systems that would provide extended service life under corrosive atmosphere.

It is an alternative to sand blasting in field applications where cost, dust, noise, and other health hazards associated with blast cleaning may restrict its use.

While the current example describes a Hypalon-Penetrant coating system capable of room temperature application and cure, other similar systems capable of curing by activation with heat may also be developed. Also, attempt would be made to extend the concept to high performance epxoy systems.

Accelerator® 808 is a commercial product of Elastomers Department and its use in the coatings hinges upon a favorable toxicity and handling assessment. Initial product application is in the field of Maintenance Paint Industry.

Filing Requested By: _____ Date: _____

R. T. Khanna

Copy to:
P. H. Pettit, Jr., Exp. Sta.
File, Exp. Sta.

(c) The said composition providing outstanding corrosion protection even on hand-cleaned rusty steel.

(d) The said composition used with or without a durable topcoat for extended service life as a protective coating.

(e) The system curing at ambient conditions.

(f) The system curing on baking.

(g) Pigments in the primer are anti-corrosive, inhibitive, and/or metal flakes.

It is possible that a number of different patent applications may be necessary to cover various embodiments of this system. Following examples would illustrate the scope of this technology:

Example 1:

Penetrant containing Accelerator® 808 (or similar compounds) dissolved in toluene in combination with at least one of the following:

a. Monomethacrylate such as BMA, LMA

b. Diacrylate such as epoxy diacrylate

c. Triacrylate such as trimethylol propanetirmethacrylate

d. A film forming vehicle.

A preferred blend is as follows:

Accelerator® 808	10
Butyl Methacrylate	60
Epoxy Diacrylate	30
Solvent Blend	150
% Solids	40
Brookfield Viscosity at 100 rpm	10 cps
Appearance	Clear
Color	Light yellowish

Penetrant is applied by brush or spray to marginally clean surfaces. Exact amount is not critical nor is the time required before the primer is applied.

Primer:

Hypalon 30 is dissolved in toluene at 20% solids. Hypalon contains "chlorosulfonated" groups on the polymer backbone, which on contact with Accelerator® 808 initiate free-radical polymerization of the monomers in the penetrant, resulting in in-situ cured film (without any mechanical mixing) chemically bonded to Hypalon 30.

A preferred formulation is as follows:

Hypalon 30	20
Toluene	80
W-128 (Al-flake) 60% Solids	22.3
% Solids (weight)	27.3
P/B	67/100

Primer is applied by brush or sprayed to a surface previously wetted with the penetrant. The surface is coated to a dry film thickness of 4-6 mils and exposed to salt spray atmosphere. No failures occur even beyond 1500 hours while panels made without penetrant show scribe blistering before 1000 hours exposure to salt spray fog. Tests are continuing.

Further development of the concept can conceivably lead to one component system such as:

1) A Penetrant-Primer that cures in-situ on exposure to light. Photo-polymerization initiator systems are being identified that overcome air-inhibition problem to an extent to make them commercially feasible.

2) A Penetrant-Primer that cures in-situ on exposure to atmospheric oxygen. Typically, the product would contain air-drying moieties and polyacrylates.

The use of a topcoat containing activating species may be optional. In a suitable formulation, such a topcoat would enhance the cure and performance of a penetrant-primer. We will continue our efforts in this area to identify a preferred patentable candidate.

RTK:ayk
4/12/77

APPENDIX VI

ACRYLIC MODIFIED PRIMERS WITH ISOCYANATE PREPOLYMERS

TITLE:

Air-Drying metal protective coatings for rusty steel and marginally cleaned (hand-cleaned) steel eliminating the need for sand-blasting.

SUMMARY:

The invention can be described in four forms:

(a) Pigmented air-drying resins (such as alkyds, epoxy esters and other polymers containing air-drying functionality) formulated with a polyacrylate/methacrylate (such as trimethylolpropanetrimethacrylate, (TMPTMA), epoxy-diacrylate (XD-9002) provide high solids primer and improved corrosion resistance when applied to marginally clean and porous rusty surfaces.

(b) A low viscosity high solids "epoxy" coating without the use of curing agents normally required in the ambient cure coatings. The term "epoxy coating" implies that the major portion (50%) of the vehicle in the dry film is derived from "bis-A epoxy" moiety. A formulated primer is fast dry and provides good protection on hand cleaned rusty steel. The absence of water sensitive amine and/or carboxyl group is expected to enhance hydrolytic resistance of the coating.

(c) A pigmented composition consisting of a cross-linked network of "alkyd-epoxy ester-acrylates" formulated from a blend of (i) air-drying alkyd, (ii) epoxy ester of air drying fatty acids and (iii) polyacrylate/methacrylates.

(d) A pigmented composition consisting of a cross-linked network of "air-drying vehicle with hydroxyl group - isocyanate prepolymer (such as Desmodur N-75, Desmodur E-21 and polyisocyanates such as MDI or TDI-based prepolymers) - polyacrylate/methacrylates.

The following examples illustrates the concepts outlined above.

Examples of (a) Reference 878E-68-1

	Parts by Weight
Dulux® 67-746	164
TMPTMA	53
Mix Ratio (by volume)	2:1
% Solids (wt.)	87.53
(vol.)	77.00
PVC	23.5
Dry Time	18-24 hrs

Corrosion Resistance excellent at 1500 hours salt spray.

Note: alkyd modified with polyacrylate.

Example of (b) Reference 878E-141-I

	Parts by Weight
Epoxy diacrylate XD-9002	1
TMPTMA	1
Epoxy Ester 786E-68	5
H-44	4
H-172 (10% in H-44)	0.5

% solids (wt. 54.5 can be increased to 70% by reformulation, clear (unpigmented), can be pigmented.

Dry Time	7 hrs

Note: epoxy coating without conventional curing agent.

Example of (c) Reference 878E-69-I

Dulux® 67-746	7.54
TMPTMA	2.44
Epoxy Ester 786E-68	5.00
H-172	0.02
H-49	5.0
% Solids (wt.)	64 can be increased to 75%
PVC	14.3%
Dry Time	4 hrs

Example of (d)

Reference: 878E-146-	I	II	III**	IV***	V**	VI**
Dulux® 67-H-43034					164	13.5
Dulux® 67-746				164		
786E-30 (air-dry oligomer)	20	20	20			
TMPTMA			20	20	20	1.45
BGDMA	20	20		33	33	
Des. E-21		20	20			
VG-Y-518	20			20	20	1.5
H-79	15	15	15			
H-72 ml	0.1	0.1	0.2			
% Solids (wt.)	73.3	80	80	87	87	
Dry time, hrs	~12	1.5				
Additional H-172 (in half the mix) ml	0.5	0.5				
Dry Time*, hours	3	0.5				
Appearance	Clear Glossy	Clear Glossy Tends to bubble in 6-10 mil builds				

*Dry time and pot life are adjustable by selecting proper concentration of the drier, retarders and inhibitors.

**Tentative composition, not tested in detail

***Optionally can add other compatible resins such as RC-66047 (or other hard, short oil alkyds) at 10-20 parts level to accelerate to lacquer dry and yet meet 70% vol. requirement.

ADDITIONAL EXAMPLES 878E-148-	I*	II*
	Parts by Weight	
Primer mill base (878E-148	90.82	90.82
Dulux® 67-H-43034 Alkyd Primer	164.0	135.0
TMPTMA Polyacrylate	33	32.1
VG-Y-518 Polyisocyanate	30	
BGDMA Dimethacrylate	40	
Des E-21 Polyisocyanate		20.0
% Solids (wt.)	85.3	85.5
(vol.) approx.	70+	70+
Dry Time, hours	6	1
Appearance	Smooth	
Gel Time, hours	>4	1

Preparation of Primer Mill Base (878E-148)

	Parts by Weight
RC-60462	18.82
H-253	11.74
H-446	5.78
H-457	2.45
VH-67552	0.38
VD-5822	1.19
H-173	0.46
Sicorin RZ	10.0
Zinc Molybdate	40.0
Total	90.82
% Solids (wt.	80.4

* Dry time and pot life are adjustable by proper selection of the driers, catalysts, retarders and inhibitors.

DISCUSSION:

Linseed oil and alkyds made therefrom with red lead or zinc chromates are commonly used primers for marginally prepared rusty surfaces. Reasonably good corrosion protection is obtained from these systems but failures are normally seen as blistering and breakdown of the film integrity because of poor chemical resistance of the film.

Corrosion protection of these systems is considerably enhanced (2X+) when these are used in combination with polyacrylate or polymethacrylate. Examples of such acrylates/methacrylates are

a) Trimethylolpropanetrimethacrylate (TMPTMA),

b) Epoxy-diacrylate (XD-9002),

c) Butane dioldimethacrylate (BDDM), and

d) Other acrylic monomers or their adducts.

The resultant formulated products show

i) improved dry,

ii) enhanced corrosion protection

iii) high solids 70% volume solids

iv) low viscosity.

The system offers wide formulating flexibility in the speed of drying and cure. Among the additives that can be used are the driers, anti-skinning agents such as oximes and isocyanate prepolymers. Nominally the dry time is adjustable between 4-16 hours by proper formulation. Excessive crosslinking functionality can result in film embrittlement and need to be balanced so that a commercially useful product can be developed. This can be done by one or all of the following schemes:

a) blending polymethacrylates with di- and mono-methacrylates

b) using soft air-drying vehicle, such as long-oil alkyds

c) adding flexibilizing additives such as nonleaching plasticizers and polyols.

The primers based on these systems normally have excellent dry adhesion to steel surfaces. Their adhesion may further be augmented by using amino-functional additives or reactive prepolymers.

PUBLICATIONS:

This is an extension of Du Pont's effort in polyacrylate modified air drying alkyds originated by Phillips Heiberger and currently followed by Ken Leavell. The invention of this patent request is that these compositions can (i) enhance corrosion resistance, (ii) yield a higher solids system and (iii) provide rapid dry coating system. It would be appropriate to examine current patent applications in this area and to include the unique performance properties identified in this application.

One patent recently issued to Celanese (U.S. 4,014,830) where the amount of polyacrylate employed was limited to less than 10% and no claim was made to improved corrosion resistance of the primer based on this technology. It would be evident from detailed examination of this application that the subject application can be subdivided for easier patentability. The unique feature in this application is the polymerization of acrylic monomers or prepolymers in thin films (10 mil) in the presence of atmospheric oxygen and improved corrosion resistance of the primer made from these vehicles.

IMPORTANCE OF THE INVENTION:

Coating rusty steel without elaborate cleaning such as blasting, abrasive grinding, polishing, and/or careful metal treatments (chromate or phosphate) has been an unattainable goal for a long time. This is an initial effort to identify systems that would provide extended service life under corrosive atmosphere.

It is an alternative to sand blasting in field applications where cost, dust, noise and other health hazards associated with blast cleaning may restrict its use.

While the current examples describe an ambient cure coating system capable of in situ and thin film cure, other systems of improved corrosion resistance but cured by activation with heat may also be developed. Also, attempt would be made to extend the concept to primers for automotive end uses.

TMPTMA is a commercial product (Rohm & Haas, and Sarotomer Chemicals) and other similar polyfunctional monomers are available. Their use in the coatings hinges upon a favorable toxicity and handling assessment. Initial product application is in the field of maintenance finishes. A successful patent application would give us significant product advantage.

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RTK:lms